JOURNAL OF ANALYTICAL CHEMISTRY
VOLUME 7 NUMBER 1 1952

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume 7, 1952

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

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152 West 42nd Street
New York 18, N. Y.

Printed in Great Britain

Annual subscription $80.00
Index 2.50

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THE SOLUBILITY OF PRECIPITATES IN THE PRESENCE OF COMMON IONS AND OTHER IONS[1)]

A. K. Babko

The Institute of General and Inorganic Chemistry of the Academy

Academy of Sciences of the USSR, Kiev

The Effect of Chemical Factors, and the Effect of the Ionic Strength on the Stability of Precipitates

The solubility of precipitates is one of the most characteristic factors to be considered in the separation of the elements, and in the many methods of determining them. Solubility depends on different factors: concentration of the common ions, the acidity of the solution, the presence of complex-forming substances, the presence of non-aqueous solvents, and the temperature and ionic strength of the solution. Unfortunately during the last 20-30 years most of the work carried out has been done on the effect of the last factor. On the other hand far too little attention has been paid to the effect of chemical factors, it being sometimes assumed that experiments based on the principle of the solubility product have no scientific significance, as if this principle were only of empirical value which is often not justified experimentally.

The relation between solubility product Lp and activity product La was considered in 1943 by A. F. Kapustinsky [1] who also showed the connection of La and Lp with the thermodynamic expression for free energy. The chief defects of work based on the study of the action of strong electrolytes are the following. There is no exact physical picture of the relationship between ionic activity and the ionic strength of the solution. The equations of Debye, Huckel and others give better agreement between theory and practice, the more empirical coefficients they introduce into these equations. Further, chemical factors are often completely ignored. Thus the effect of excess common ions on the solubility of a precipitate is considered exclusively in the light of Debye and Huckel's theory. Meanwhile it is completely obvious that complexes are formed by interaction between certain compounds, as has been shown, e.g. between $PbCl_2$ and NaCl, AgI and KI (and with $AgNO_3$), and $PbSO_4$ with acetates, etc. Complex ions are also formed by the interaction of highly charged ions with precipitates, [e.g. Zr^{4+} with $Zr(C_2O_4)_2$ to form $ZrCr_2O_4^{2+}$, etc.], nevertheless, these reactions

1) Reported at the Conference on Classical Method of Chemical Analysis held in Moscow 14-17 November 1951.

and numerous other chemical reactions are not taken into consideration, the results being attributed to the effect of strong electrolytes.

Finally the effect of the ionic strength of solutions is comparatively small. Even for ionic concentrations where maximum deviation between the numerical values of the concentrations and ionic activity is observed, the change in solubilities is rather small. Thus, for the most common precipitates of the 2-2 valency type ($BaSO_4$, CaC_2O_4, etc.,) the following relationship can be established. The relation between La and Lp is expressed by the equation [1]:

$$Lp = \frac{La}{f^2},$$

where f is the activity coefficient. The neutralized activity coefficient for doubly charged ions for an ionic strength $\mu = 0.1$ amounts to $f = 0.25$ [2]. Thus for $\mu = 0.1$, the solubility product increases to the value given by

$$Lp = \frac{La}{f^2} = 16La,$$

i.e. to 16 times the solubility in the absence of other electrolytes. This calculation shows that for accurate experiments, it is essential to consider the effect of other electrolytes. The simplest method of doing this is to insure a constant ionic strength in any series of experiments; obviously, in this way Lp will be constant. Such conditions correspond very well with normal analytical conditions, since in order to dissolve the substances being examined (alloys, silicates, etc.), a considerable amount of acid, alkali, or other reagents is used. Precipitation therefore usually occurs in the presence of an appreciable, and sufficiently constant amount of other electrolytes. Thus the effect of the ionic strength can be easily eliminated, and be made constant, just as is usually done with the temperature, which is of no less importance than the ionic strength.

Consequently, there is no basis for assigning any exceptional importance to the non-chemical effect of other electrolytes. Even in the least favorable cases the effect can change the solubility only ten times. On the other hand, chemical factors (presence of common ions, pH of the solution, complex compound formation, etc.) can change the solubility by a factor of 10^{20} or more. There is not a single analytical method based on the effect of strong electrolytes; the majority of methods used for separating and estimating elements is based on the effect of different chemical factors. This practical criterion shows that in the study of the solubility of precipitates, chief attention should be given to the questions of the influence of common ions, the acidity of the solution, complex compound formation, and non-aqueous solvents.

The Chemical Effect of an Excess of Precipitant on the Solubility of the Precipitate

The best known and most often used consequence of the solubility product principle, is the lowering of the solubility of a precipitate on the addition of excess of a common ion, i.e. usually an excess of precipitant. However, this only holds in those cases where the formation of a precipitate BA is the only form of chemical reaction between a cation B and an anion A. In the majority of cases, however, the precipitate BA is only one of several forms of the product of reaction between the components. In all cases the use of excess precipitant decreases the concentration of the precipitated ion. Nevertheless, when this occurs, it is only in certain cases that the precipitated ion is transferred to

the solid phase of the same composition. In other cases, an excess of precipitant leads to the formation of new chemical compounds.

To one degree or another, all types of chemical interaction between precipitate and excess precipitant are known; precipitation reactions, i.e. the formation of other precipitates (besides PA), acid-base reactions, oxidation-reduction reactions, and complex compound formation.

An excess of precipitant can lead to a change in the composition of the precipitate, i e. to the formation of a new solid phase. Thus precipitates of phosphates can be formed, the composition of which vary with the amount of precipitant (e.g. $CaHPO_4$ and $Ca_3(PO_4)_2$,etc. A number of characteristic cases of the formation of solid phases of different chemical composition for different amounts of excess precipitant has been studied by I.V.Tananaev and coworkers [3] for the case of metallic ferrocyanides.

Interactions of an acid-base character are also known. Thus, in certain cases, in the presence of excess metal cations, basic salts are formed. Excess of precipitant – multibasic acids – at low concentrations leads to a decrease in the solubility of the precipitate, while at high concentrations it dissolves the precipitate with the formation of acid salts (e.g., the formation of hydrocarbonates, hydrosulfides, etc.)

Nevertheless, of all the possible forms of chemical reactions between precipitate and excess precipitant, the most important is that of complex compound formation. It is well known that a large number of compounds, despite their low solubilities, can not be used analytically as precipitates, owing to their solubility in excess precipitant. Such, e.g., are the iodides of bismuth and mercury, the oxalates of copper, bivalent iron, and zirconium and the majority of metallic cyanides, etc. In the precipitation of many precipitates, it is necessary to insure conditions, such that the concentration of excess precipitant is not very high. Thus, e.g. $Al(OH)_3$ can be precipitated by alkali hydroxides just as well as by ammonium hydroxide, but excess alkali hydroxide dissolves the precipitate with the formation of aluminates. In the precipitation of silver halides, a large excess of precipitant also leads to an increase in the solubility of the precipitate, etc.

Complex compound formation between excess precipitant and precipitate is one of the chief handicaps in the application of precipitates in analysis. Complex compound formation can be used in some cases for dissolving precipitates; unfortunately, although these reactions are very well known, they have been little studied.

Cases of increased solubility of the precipitate owing to the effect of excess anions are more common; in such cases complex anions are formed which are saturated (or near saturated) in the coordination sense. Nevertheless, detailed study of complex compound formation by a number of investigators in recent years has shown that such reactions proceed stepwise. In the chemistry of complex compounds the best known compounds are coordinately saturated complexes. However, those forces which lead to the formation of coordinately saturated complexes, in other conditions lead to the formation of stable,although coordinately unsaturated, complexes. If for any central ion B and a coordinated ion (usually an anion) A, a coordinately saturated compound BA_n is known, then a detailed investigation always shows that a whole series of coordinately saturated[1])

[1]) The central ion of these complexes may be coordinately saturated by combining with solvent molecules. The term "coordinately saturated" is used here in its usual sense for denoting compounds in which the central atom B is linked with an incomplete number of the coordinated ions A.

complexes exists in solution, which are related stepwise.

If one of the members of this series of complexes $\underline{BA}_m$, where $\underline{m}$ is less than $\underline{n}$, has a low solubility, then the properties of such a precipitate will have specific characteristics. By the addition of excess of a common ion $\underline{A}$, the solubility of the precipitate will increase as the result of the formation of complexes such as $\underline{BA}_{m+1}$, $\underline{BA}_{m+2}$ ... $\underline{BA}_n$. In addition, in consequence of what has been noted above, it should be expected that this precipitate will dissolve also in the presence of excess cations forming complexes of the series $\underline{BA}_{m-1}$, $\underline{BA}_{m-2}$, etc. Experiment shows that this actually occurs. Precipitates which dissolve in excess of their own (common) anions, will also dissolve in an excess of common cations.

One of the most widely studied precipitates in this connection is mercuric iodide. HgI_2 is one of a series of complexes HgI^+, HgI_2, HgI_3 and HgI_4^{2-}. Morse [4] who demonstrated the formation of all the complexes in this series, also determined the constants in the stepwise dissociation of $HgCl_4^{2-}$. The solubility of HgI_2 in excess of common anions is well known. KI dissolves almost an equivalent amount of HgI_2. In addition, HgI_2 dissolves in excess of $Hg(NO_3)_2$, forming the complex HgI^+:

$$HgI_2 \text{ (solid)} + Hg^{2+} = 2HgI^+.$$

According to Morse, 48 g of HgI_2 (i.e., ca. 0.105 mole) can be dissolved in 1 liter of N $Hg(NO_3)_2$.

AgI dissolves both in excess KI and in excess $AgNO_3$, forming the complex cation Ag_2I^+. Similar reactions can be observed with other precipitates (BiI_3, etc.)

The solubilities of the oxalates of the rare earths and of thorium are of great importance in the determination of these elements. In work published on the solubility of rare earth and thorium oxalates, and also in published methods for the analyses of these elements, it is emphasized that these oxalates must only be precipitated by oxalic acid, and not by the oxalates of the alkali metals, since the latter form soluble complexes. The rare earth oxalates in this connection are therefore analogous to $Al(OH)_3$, which must be precipitated by a weak base, NH_4OH, since it will dissolve if there is a considerable excess of OH^- ions present. The slightly dissociated oxalic acid (in the presence of HCl) gives a low concentration of $C_2O_4^{2-}$ ions, which are sufficient for the quantitative precipitations of the rare earth oxalates. On addition of the highly dissociated oxalates of the alkali metals however, soluble oxalate complexes of the rare earths and thorium are formed.

In view of the properties noted above of precipitates of a complex character, it is to be expected that rare earth oxalates would also dissolve in excess of common cations. In fact, the oxalates of cerium and thorium dissolve easily (particularly on heating) with the formation of complex cations $Ce_2O_4^+$, $ThC_2O_4^{2+}$, etc., when the precipitates are treated with solutions of cerium or thorium nitrates, respectively. Similar reactions with the iodates of certain rare earths are sometimes used as a proof of the incorrectness of the solubility product principle. However, a study of the effect of other electrolytes shows that if these electrolytes do not react chemically with the precipitate, then their effect will be insignificant (for the same ionic strength of the solution). The solubility of precipitates as a result of the formation of complex cations is of no less significance than the solubility owing to the action of excess anions, although the first group of reactions has been studied to a considerably less extent. The enhanced solubility of the oxalates of thorium, and of the rare earths, in the presence of salts of aluminum, and particularly of iron, is due

to the formation of complex cations of the type $AlC_2O_4^+$, $FeC_2O_4^+$, and also $ThC_2O_4^{2+}$ etc. Precipitated CuF_2 dissolves easily in excess $AlCl_3$, the complex cation AlF^{2+} (or AlF_2^+) being formed.

Changes in the Solubility of a Precipitate of a Complex Character in the Presence of Common Ions

The examples of complex formation between precipitates and common ions in solution noted above, necessitate consideration of the general question of the change in solubility owing to the action of excess common ions.

HgI_2 can be taken as a characteristic example of such a system in which complex formation occurs. As mentioned above, a series of complex groups HgI^+, HgI_2, HgI^{3-} and HgI_4^{2-} can be formed in the system $KI - Hg(NO_3)_2$ in solution, depending on the absolute and relative concentrations. According to experimental results obtained by Morse [4] which have been somewhat modified by the present author [5], the formation of complexes in the system $Hg^{2+} - I^-$ (in solution) is characterized by the following relations for the stepwise dissociation constants.

$$K_1 = \frac{[Hg^{2+}][I^-]}{[HgI^+]} = 10^{-14}; \qquad K_2 = \frac{[HgI^+][I^-]}{[HgI_2]} = 10^{-10.3};$$

$$K_3 = \frac{[HgI_2][I^-]}{[HgI_3^-]} = 10^{-5.3}, \qquad K_4 = \frac{[HgI_3^-][I^-]}{[HgI_4^{2-}]} = 10^{-0.7}.$$

The solubility of HgI_2 in water is $1.4 \cdot 10^{-4}$ mole per liter. On the basis of these results, it is possible to calculate the state of HgI_2 in a saturated aqueous solutions

The principle of calculation is similar to the well known formula for the pH of an acid salt and consists of the following. The dissociation of HgI_2 in solution, in accordance with the values of the stepwise dissociation constants, proceeds mainly according to the equation $2HgI_2 = HgI^+ + HgI_3^-$; the ions Hg^{2+} and I^- are formed only to an insignificant extent.

So that the solution remains electrically neutral

$$[HgI^+] = [HgI_3^-].$$

From the relations for K_2 and K_3, it is found that

$$[HgI^+] = \frac{K_2 \cdot [HgI_2]}{[I^-]} \text{ and } [HgI_3^-] = \frac{[HgI_2][I^-]}{K_3}.$$

Comparing these equations, it follows that: $[I^-]^2 = K_2 \cdot K_3$, from which

$[I^-] = \sqrt{K_2 \cdot K_3} = 10^{-7.8}$.

From the last relation and K_2 $\frac{[HgI^+]}{[HgI_2]} = \frac{K_2}{[I^-]} = \frac{10^{-10.3}}{10^{-7.8}} = 10^{-2.5}$,

i.e. the concentrations of HgI^+ (and HgI_4^{2-}) are very small in comparison with the concentration of the molecules of HgI_2, therefore it can be assumed that the concentration of the non-dissociated part of the HgI_2 is equal to the total solubility, i.e., $[HgI_2] = 1.4 \cdot 10^{-4}$. Using this value, and also the concentration of $[I^-] = 10^{-7.8}$ calculated above, it is possible by the usual methods (by means of the relations of the dissociation constants) to find the concentrations of the

residual components of the system. Omitting the details of calculations, the results are as follows (approximately).

In a saturated solution of HgI_2, the following concentrations of the different complexes are in equilibrium: $[Hg^{2+}] = 3\cdot10^{-13}$; $[HgI^+] = 5\cdot10^{-7}$; $[HgI_2] = 1.4\cdot10^{-4}$; $[HgI_3^-] = 5\cdot10^{-7}$; $[HgI_4^{2-}] = 4\cdot10^{-14}$; $[I^-] = 1.4\cdot10^{-8}$.

The existence of such a complicated system in equilibrium in a saturated solution is not exceptional. Analogous results can be found in the literature for other electrolytes, e.g., PbI_2, etc. The equilibrium system in a saturated solution of Na_3AlF_6, is undoubtedly even more complex [6]. In this connection, it is essential to ask how to express the solubility product of a precipitate of a similar type. In a saturated solution of HgI_2, five types of ions can be found apart from the undissociated molecule of HgI_2. The concentration product of any pair of ions which can form HgI_2 by interaction, will be a constant, and can with equal justification be regarded as the solubility product. Thus, the precipitate of HgI_2 can be formed by the interaction of $Hg^{2+} + 2I^- = HgI_2$. The constant for this reaction is given by

$$\underline{Lp}_1 = [Hg^{2+}]\cdot[I^-]^2 = 6\cdot10^{-29}.$$

The formation of a precipitate is also possible as a result of the reaction $HgI^+ + I^- = HgI_2$. The second "solubility product" corresponds to this equation:

$$\underline{Lp}_2 = [HgI^-]\cdot[I^-] = 7\cdot10^{-15}.$$

Other relations for the "solubility product" are also possible, each of which will have a constant value in a saturated solution. The question is which of these expressions will be the "true" solubility product. This question has no real significance for a system in which complex formation occurs.

In a system where there is no complex formation, it is possible to calculate the solubility of a precipitate in the absence of common ions, by means of the solubility product. In a given case, as can be seen from the values given above, the solubility is determined not by ions, but by the presence of undissociated molecules of HgI_2.

In a system where there is no complex formation, it is possible to calculate the decrease in solubility, on increasing the concentration of one of the ions, from the values of the solubility product. In the case considered, even complete elimination of the ionic solubility cannot essentially lower the solubility of the precipitate, since the concentration of the precipitate ions is negligible in comparison with the concentration of molecules of HgI_2^-. Moreover, the addition of complex ions (such as HgI_3^-) has no practical significance, while the introduction of simple ions (Hg^{2+} and I^-) will increase the solubility. The relations $\underline{Lp}_1$, $\underline{Lp}_2$, etc., given above characterize the free energy of formation of the solid phase from the corresponding ions. However, it is neither one nor the other of the relations for the solubility product which is important for the characterization of the equilibrium between the solution and a precipitate of complex nature. A knowledge of these values (and also of the solubilities of the precipitate) enables the effect of the common ion to be calculated.

For the precipitate of HgI_2 (and other precipitates of a similar type) the solubility in the presence of excess common ions can be found from the following equations. The solubility in the presence of excess anions is determined by the formation of HgI_3^- according to the reaction $HgI_2 + I^- = HgI_3^-$.

From which, taking into account the third dissociation constant, the following relation is obtained:

$$[HgI_3^-] = \frac{[HgI_2]\cdot[I^-]}{K_3}$$

The solubility in the presence of excess cations is determined by the formation of HgI^+ according to the reaction $HgI_2 + Hg^{2} = 2HgI^+$.

The solubility as a function of the varying concentration of the cations $[Hg^{2+}]$, the constant value of the molecular solubility $[HgI_2]$, and dissociation constants of the complexes, can be calculated from K_1 and K_2 by elimination of the value of $[I^-]$:

$$[HgI^+] = \sqrt{\frac{K}{K_1}[HgI_2][Hg^{2+}]} = \sqrt{\frac{K}{K_1}\ 1.4\cdot10^{-4}\cdot[Hg^{2+}]}$$

By direct substitution of the values in the above equation, it is possible to show that the solubility for a 0.1 excess of ions will be $[HgI_3^-] = 3$, i.e. in practice, the solution of HgI_2 in KI proceeds until almost all the latter is used up. For an equal excess of cations, the solubility will be less; for $[Hg^{2+}] = 0.1$ mol., $[HgI^+] = 0.2$ (this approximates to Morse's results).

The minimum solubility for precipitates of the type of HgI_2, which occurs in the absence of excess common ions appears to be in complete contradiction with the properties of precipitates which cannot form complexes.

Actually, as was shown above, the solubility of HgI_2 is determined chiefly by the presence of molecules.[1] Consequently the lowering of the concentration of HgI^+ or HgI_3^- ions in the presence of common ions, is generally of no appreciable significance. On the other hand, complex formation increases the solubility even at very low concentrations of excess common ions, e.g., it is possible to calculate the concentration of common ions, for which the solubility doubles. This, obviously, will take place if the "additional solubility" i.e., the concentrations of $[HgI^+]$ or $[HgI_3^-]$ become equal to the concentrations of molecules of $[HgI_2]$, in a saturated solution. For the condition where $[HgI^+] = [HgI_2]$, then $[I^-] = K_3 = 5\cdot10^{-6}$; while for $[HgI^+] = [HgI_2]$, $[Hg^{2+}] = \frac{K_1}{K_2}$, and $[HgI_2] = 3\cdot10^{-8}$. Thus even at a very low excess of common ions the solubility increases to double the value of the solubility in pure solvent.

For many precipitates the capacity of complex formation is not so manifest as for HgI_2. Thus, according to some results in the literature and to the author's calculations, the solubility of PbI_2 is determined chiefly by the presence of Pb^{2+} and I^- ions, in addition to which there are only 10% PbI^+ ions and even less PbI_2 molecules. The solubility of such compounds, which seem to be a more general type of precipitate, can be characterized as follows. The curve relating the total solubility of the precipitate to the concentration of an excess of anions of the same kind, may be expressed as the sum of two curves for the different kinds of solubility. One form of solubility ($\underline{X}_1$) is determined by the presence of simple ions, and can be calculated by the normal method from the solubility product. This part ($\underline{X}_1$) of the total solubility decreases on adding similar ions.

The other form of solubility ($\underline{X}_2$) is determined by the formation of complexes

---

[1]) Results collected in handbooks on solubilities also indicate that the solubility of HgI_2, as determined gravimetrically, is a few hundred times the solubility calculated from electro-conductivity measurements.

with common ions. This form of solubility increases on introducing excess of common ions.

The total solubility will be equal to $S = X_1 + X_2$. For a small excess of anions X_2 will be small (complex formation is insignificant), and the solubility will be determined chiefly by the value of X_1. On increasing the concentration of the excess of common anions, the value of X_1 decreases in accordance with the solubility relation. On the other hand, the value of X_2 gradually increases (particularly as the value of [A] approaches the value of K_3) and finally becomes greater than the value of X_1. Thus, the relation between total solubility and the concentration of excess common anions is expressed by a curve with a minimum. From what has been said above, it is obvious that the minimum will occur when $X_1 = X_2$. Korenman [7] came to similar conclusions for the solubility of PbI_2 in KI. Lanford and Kiel [6], during detailed investigation on the solubility of PbI_2 in KI, also found a similar minimum (at 0.1 M KI). If the dissociation constant of the complex

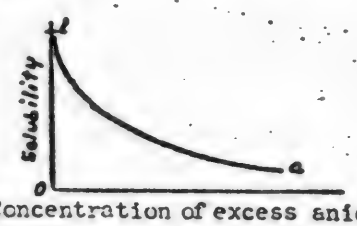
$$K_{BA_3} = \frac{[B^+][A^-]^3}{[BA_3^-]}$$

, then according to Korenman's calculations the solubility minimum will occur at $[A^-] = \sqrt[3]{K_{BA_3}}$. In connection with the results given above for the stepwise character of the formation of the complexes, the relation between the solubility of the precipitate and excess of cations will be characterized in similar cases by a curve having a minimum.

The General Characteristic of the Effect of Common Ions on the Solubility of Precipitates, when Complex Formation Occurs

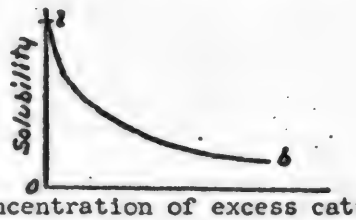
From the characteristics of the equilibrium between precipitate and excess of common ions considered above, it is possible to make a number of general conclusions. The normal character of a precipitate - the solubility product - can be used for calculating the solubility in the presence of excess common ions, only when there is no complex formation. For many precipitates, on the other hand, the formation of complex anions and cations by the action of excess common ions is, to one degree or another, characteristic. In order to calculate this effect, it is essential to know the values of the stepwise dissociation constants of all the complexes formed in the system. These values are known for only a few cases. Such calculations, though of interest in individual typical cases, cannot be used in the study of the formation and solution of many precipitates. It is more expedient therefore to characterize such complex equilibriums on the basis of physico-chemical analysis.

Usually during investigation of the effect of common anions on the solubility of the precipitate, the results are expressed by a digram of the type shown in Fig. 1.



Concentration of excess anions A.

Fig. 1.



Concentration of excess cations B.

Fig. 2.

Solubility is plotted along the ordinate, and the concentration of excess A anions along the abscissa. The point O corresponds to a pure precipitate in the absence of excess common ions, and the ordinate O1 represents the solubility of the precipitate under these conditions. If, e.g. the precipitate does not form, or only forms an unstable complex with excess A anions, then the relation between the solubility of the precipitate and the concentrations of A anions is depicted by the lina 1a curving downward.

The results of investigating the solubility of a precipitate in the presence of excess common cations are usually expressed in the manner shown in Fig. 2. The concentration of ions and the solubility of the precipitate are plotted against the abscissa and ordinate respectively. In the absence of any appreciable complex formation, the relation is expressed by the descending curve 1b. When however, this method is used for plotting the results, such properties of the precipitate as are closely related and are determined by the chemical nature of the precipitate, are considered separately. During the precipitation of any precipitate, there exists initially a system with an excess of one of the anions, while toward the end of precipitation (after the addition of an equivalent amount of precipitant) the system contains an excess of the second ion. Sometimes the same precipitate (e.g. AgCl) can be used for determining either the cation or the anion, under different conditions. Therefore it is worth while combining the two types of diagram so as to consider in a general way the effect of both ions on the solubility of the precipitate. To do this, Fig. 2 is turned around the ordinate through 180° and placed back to back to Fig. 1, to give a diagram of the type of Fig. 3, which under certain additional conditions [1]) will be a typical diagram of physico-chemical analysis, and characterizes the relation between the composition and a property of the system. The ordinate represents the most important property of a precipitate – its solubility – while the abscissa represents the different possible concentrations of excess of both common ions.[2])

The formation of a precipitate in a saturated solution containing excess ions of both types can be effected simply by mixing a solution of electrolyte containing the cation B with a solution of an electrolyte containing the anion A. The original solutions can be prepared of equal molarity and can then be mixed in different amounts, so that the sum of the volumes of the solutions remains a constant. In reactions between ions of the same valency, a precipitate BA is normally obtained. If, e.g. 50 ml of a salt of B is mixed with 50 ml of a solution of a salt of A (solutions of equal molarity), then a system is obtained in which the precipitate is completely free of excess of common ions. The geometrical position of a mixture composed of equal volume of A and B correspond to point O on the abscissa of the composition-property diagram (Fig. 3). The ordinate at this point, O1 represents the solubility of the precipitate in the absence of common ions. It is obvious that O1 (Fig. 3) in the physical sense corresponds to similar ordinates in Figs. 1 and 2.

If solutions of the reactants are not mixed in equivalent amounts, then the mixture will correspond to different points along the abscissa. Systems of precipitate BA in the presence of different concentrations of excess anions A lie to the right of O, while systems of precipitate BA in the presence of different concentrations of excess common cations B lie to the left of O. The relation between solubility and concentration of excess ions is expressed by the charac-

[1]) It is the relative and not the absolute values of the concentration or volume which are plotted on the abscissa. The scale is also changed.
[2]) I.V.Tananaev used a similar diagram.

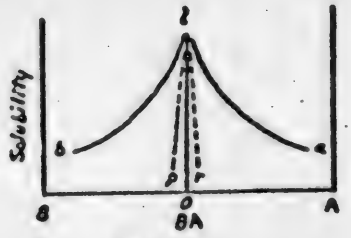


Fig. 3

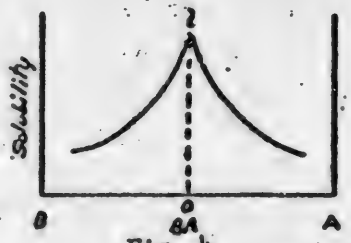


Fig. 4

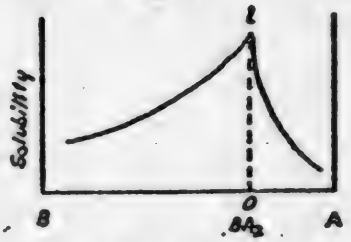


Fig. 5

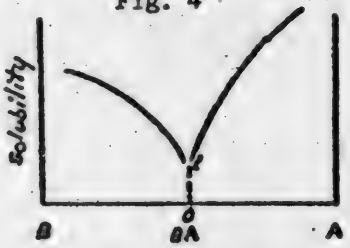


Fig. 6

teristic curve b1a. The curvature of the lines b1 and 1a depend on the choice of scale and units of measurement on the coordinate axes. For general characterization of a precipitate and also for the classification of precipitates, the question of scale is immaterial, and it is possible to use an arbitrary scale, which only indicates the principal trend of the relation.

The necessity of classifying precipitates according to the character of the effect of similar ions has been remarked on in the literature, e.g. in Golovatov's work [9]. Similar ideas regarding the various relations between solutions and excess of common ions have been put forward by I. V. Tananaev [10]. However, in accordance with the results given above, the solubilities of a series of precipitates in the presence of excess common ions is not connected with their high valency, since this is observed for such precipitates as AgCN, HgI_2, etc.,. The increase in solubilities is determined by chemical interaction with the formation of complex ions. On the basis of the results of an experiment represented on a diagram of the type of Fig. 3, it is possible to determine the character of the interaction between the precipitate and each of the common ions, and to simplify the calculation of the different constants (Lp and K complex). Finally, the application of such diagrams, with the help of additional curves (e.g., the dotted lines 1p and 1r), enables observations of the change in composition of the solid phase, owing to the formation of mixed crystals, etc., to be made.

According to the character of the effect of the common ions it is possible to distinguish four types of precipitates, to which characteristic forms of the composition-property diagram correspond.

1. The absence of complex formation between ions of the precipitate. This type of precipitate is the "ideal" one for use in analysis, since excess of common ions decreases the solubility of the precipitate, in complete agreement with the relation Lp. This curve is characterized by a sharp maximum at the point corresponding to the composition of the precipitate (Fig. 4). The form of the curve depends on the choice of scale (simple or logarithmic) and also on the composition of the precipitate. In the case of a precipitate of composition BA both branches of the curve are symmetrical (Fig. 4); for a composition BA_2 the excess of anions decreases the solubility more than an excess of cations, Fig. 5.

2. Strong complex formation between precipitate ions, in which the precipitate is a compound which is unsaturated in the coordination sense (Type HgI_2). In this case the curve has a form directly opposite to the previous curves. A point on the curve 1, corresponding to the precipitate, i.e. to the absence of excess common ion, represents the minimum solubility (Fig. 6). Excess of each of the components increases the solubility.

3. Strong complex formation, in which the precipitate is a compound saturated in the coordination sense. The relation between the solubility of cryolite, Na_3AlF_6, and the concentration of aluminum and fluorine ions can be taken as a typical example of this class.[1] If there is a complex group, e.g. Ba_2, in this precipitate (for a maximum coordination number for B of 4), then the relation will have the form illustrated in Fig. 7. Excess of anions A cannot lead to the formation of new complexes, and will therefore lead to a sharp decrease in the solubility of the precipitate. On the other hand, excess of ions B will react with the precipitate, forming coordinately unsaturated complexes BA_3, BA_2 and BA, as a result of which the solubility of the precipitate will increase.[2]

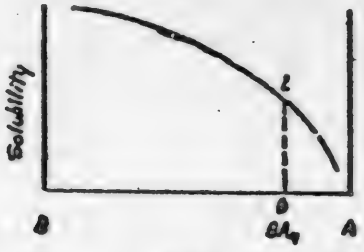


Fig. 7

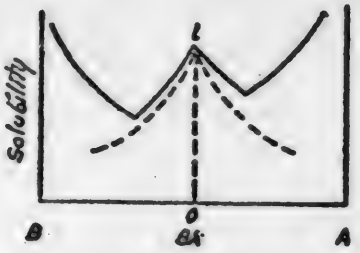


Fig. 8

4. Weak complex formation between precipitate ions. It is apparent that most real precipitates belong to this class. In general, the relation between precipitate solubility and excess common ions is represented by a curve with a maximum in the absence of common ions, and with two minimums in the presence of excess common ions (Fig. 8). For a low excess of common ions there is a decrease in solubility of the precipitate, although the decrease is not so great as would be expected on the basis of the usual application of the solubility product (dotted line, Fig. 8). For a large excess of common ions, complex formation becomes the dominant process and the solubility begins to increase. This type of common ion effect is observed for PbI_2 in the presence of excess KI, and in many other cases.

When complex formation is very weak, the minimums can lie very near to the ordinate. In some cases, when the solubility of the original salt containing B and A is restricted, the minimums cannot be observed at all; however, the solubility will be slightly higher tha that calculated from the normal solubility product (La). In such cases, the general expression for solubility product can be used for approximate calculation, but only within the limits of concentration, corresponding to the interval between the two minimums on the curve.

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1) The complete relation between the concentrations of all the ions of such a precipitate, i.e. the concentrations of Na^+, Al^{3+} and F^+, must be expressed by a ternary diagram.

2) Thus, the solubility of cryolite in aluminum salts, the solubility of the hydroxyquinolates of a series of multivalent metals in the presence of an excess of the cations of these metals, etc. are well known.

SUMMARY

The effect of common ions and other ions on the solubility of precipitates has been considered The ionic strength of the solution has some effect, but it is not large, and can be eliminated by using solutions of equal ionic strength, which correspond to practical analytical conditions. The most important effect is that of the chemical interaction between solid phase and ions in solution.

The effect of common ions on the solubility of the precipitate has been considered, when complex anions and cations are formed in the presence of excess precipitant. For precipitates which in their chemical character are one of a series of stepwise complexes in the system B cations – A anions, the solubility product is not single valued and cannot be use for the calculation of solubility.

The importance of using the principles of physicochemical analysis for characterizing the changes in solubility owing to the action of excess of similar ions has been pointed out. For this purpose, a diagram of composition against property can be used, in which the components of the composition are the solutions of the reacting ions, while the solubility of the precipitate is taken as the most important property of the system. On this basis, precipitates can be divided into four classes: 1) the absence of complex formation is characterized by maximum solubility at the equivalence point; 2) strong complex formation, characterized by minimum solubility at the equivalence point (in the absence of excess common ions); 3) complex formation, under conditions in which the precipitate is a coordinately saturated compound, in this case excess common anions, decreases the solubility, while excess common cations increases the solubility; 4) the solubilities of a large number of precipitates is expressed by a curve with a maximum in the absence of common ions, and with two minimums for a definite excess of each of the common ions.

LITERATURE CITED

[1] A. F. Kapustinsky. J. Appl. Chem. 16, 50 (1943).

[2] Yu. Yu. Lure, Notebook for Chemists.

[3] I. V. Tananaev, J. Anal. Chem. 1, 224 (1946); 4, 136 (1949).

[4] H. Morse, Z. phys. Chem. 41, 731 (1902).

[5] A. K. Babko, Jubilee Collection, Acad. Sci., USSR, 2, 136 (1942).

[6] I. V. Tananaev, J. Gen. Chem., 7, 2437 (1937).

[7] I. M. Korenman, J. Gen. Chem., 16, 157 (1946).

[8] O. Lanford, S. Kiel, J. Am. Chem. Soc. 63, 667 (1941).

[9] R. N. Golovatyi, J. Appl. Chem. 13, 86 (1940).

[10] I. V. Tananaev, Bull. Section Phys.-Chem. Analysis, Acad. Sci. 20, 277, 1950.

Received December 12, 1951

PHYSICO-CHEMICAL ANALYSIS OF SYSTEMS OF IMPORTANCE IN ANALYTICAL CHEMISTRY[1)]

XX. THE SOLUBILITY OF PRECIPITATES IN COMPLEX (REAL) ANALYTICAL SYSTEMS

I. V. Tananaev, I. B. Mizetskaya and A. D. Vinogradova

Institute of General and Inorganic Chemistry, USSR Academy of Sciences

The present work is a continuation of the authors' work on the study of the solubility of $PbSO_4$ in solutions of different electrolytes, the ions of which are the same as, or differ from those of the precipitate, and the cations of which are of different valency [1]. The noteworthy feature of the systems $PbSO_4$ – $Th(NO_3)_4$ – H_2O and $PbSO_4$ – $Th(NO_3)_4$ – Li_2SO_4 – H_2O, which is considered in the present article, is the presence of the nitrate of a quadrivalent cation. As far as the authors are aware there is no description of these systems in the literature, neither are there any experimental results relating to the errors which arise when calculating solubility on the basis of the constancy of La (the activity product), and the values of the activity coefficients are calculated from the Debye-Huckel equation. In so far as firstly the ionic strength of the solution is taken into account in the Debye-Huckel equation, while secondly the chemical interaction between the dissolved ions and precipitate is neglected, it is to be expected that disagreement between experiment and theory will be particularly large in the systems considered. The first is determined mainly by hydrolysis and incomplete electrolyte dissociation in solution, while the second is determined by the enhanced chemical activity usually observed for multivalent cations, which form chemical bonds of varying stability with the majority of anions. The nitrate of thorium was chosen as the quadrivalent cation because aqueous solutions of this salt are stable without the addition of acid. Lithium sulfate was chosen as the electrolyte containing a common ion, because as was shown previously [2, 4], $PbSO_4$ in the presence of lithium ions does not change its composition, when it comes into contact with a solution containing excess sulfide ions.

The determination of the concentration of lead in the saturated solutions was made by the use of a Chromate-iodometric method with preliminary precipitations of lead sulfide from tartaric acid solution.

In experiments on the determination of the solubility of $PbSO_4$, the concentrations of $Th(NO_3)_4$ varied from 0.0001 to 0.1 molar, for a constant concentration of Li_2SO_4 in a given series of experiments. Three lots of systems were investigated in which the concentrations of Li_2SO_4 were 0.001, 0.01 and 0.1 molar; one series was done in the absence of Li_2SO_4.

The activity coefficients according to the Debye-Huckel equation (second approximation) were calculated on the assumption of the constancy of La in all cases, on the lines of a method worked out previously. The necessary values of a were found by starting not from 0.1 and molar solutions of the electrolyte (as before) but from 0.01 and 0.1 molar solutions of $Th(NO_3)_4$ respectively.

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1) Report read at the Conference on Classical Methods of Chemical Analysis held in Moscow 14-17 Nov. 1951.

TABLE 1

The Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ at 25° C

$Th(NO_3)_4$ molar	Li_2SO_4 = 0.0 molar					Li_2SO_4 = 0.001 molar				
	Pb molar	$La_{PbSO_4} \cdot 10^8$	$La_{PbSO_4} \cdot 10^8$ For a equal to			Pb molar	$La_{PbSO_4} \cdot 10^8$	$La_{PbSO_4} \cdot 10^8$ For a equal to		
			3.04	4.86	0.27			3.04	-4.88	-0.26
0.0001	8.18	66.9	37.8	33.9	36.5	3.32	44.2	23.5	19.8	21.6
0.001	22.4	502	163	96.9	137	13.5	317	125	63.1	88.4
0.01	103	10600	835	1.62	1090	84.2	7930	644	1.62	227
0.1	289	83500	702	0.059	1.62	276	78900	665	0.063	1.62

From Table 1, it is obvious that $Th(NO_3)_4$ strongly increases the solubility of $PbSO_4$, the solubility in 0.1 molar $Th(NO_3)_4$ being 200 times that in pure water. This increase is considerably more than was found previously for $Al(NO_3)_3$ [1]. In the presence of Li_2SO_4 the effect of $Th(NO_3)_4$ on the solubility of $PbSO_4$ varies with the concentration of the Li_2SO_4, being less the greater the concentration of Li_2SO_4.

Fig. 1 (given in two scales for convenience) and particularly Fig. 2 illustrate this very graphically. Only in 0.1 molar Li_2SO_4 does the solubility of $PbSO_4$ approach the value characteristic for pure water, although this is true only for concentrations of $Th(NO_3)_4$ not higher than 0.01 molar; for 0.1 M $Th(NO_3)_4$ the solubility of $PbSO_4$ is still 10 times that in water. For low concentrations of Li_2SO_4 the solubility of $PbSO_4$ increases sharply, as shown in Fig. 2 by the dotted lines, which are lines of equal concentrations for $Th(NO_3)_4$. This is especially marked for lines of equal concentration for 0.1 molar $Th(NO_3)_4$. As can be seen from Table 1 the calculation of La_{PbSO_4} did not give good results. It follows therefore that in systems of the type considered, the formulas used do not give correct values for the activity coefficients without which the principle of the constancy of Ia cannot be used. The negative value of a which is devoid of any physical meaning, is characteristic.

The above deviations are explained by the presence in the system of a clearly expressed chemical affinity, manifested in the formation of slightly dissociated ions, apparently of the type of $ThSO_4^{2+}$. It is therefore more correct to calculate the solubility of $PbSO_4$ from the dissociation constant of such ions, the results obtained being superior to those obtained by calculations based on the use of the activity coefficients of the dissolved precipitate, which as a rule (particularly in complex systems) are unknown and are difficult to determine. In the present work, calculations based on this principle were not made because of insufficient experimental data for intermediate concentrations of $Th(NO_3)_4$.

On the other hand it should be noted that the solubility diagram adduced, enables the solubility of $PbSO_4$ to be found for any part of the system studied, with a fairly close approximation to the true value. The diagram can be used for practical purposes in cases where it is necessary to precipitate lead in the presence of multivalent ions.

The Solubility of Precipitates Under Real Analytical Conditions

The composition of solutions in systems which are dealt with in the course of chemical analysis is usually complex. Ions both common to and different from

TABLE 1

The Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ at 25°C

Li_2SO_4 = 0.01 molar						Li_2SO_4 = 0.1 molar			
		$La_{PbSO_4} \cdot 10^8$ For a equal to				$La_{PbSO_4} \cdot 10^8$ For a equal to			
		3.04	-4.11	-0.186		3.04	-3.73	0.355	
1.25	126	21	14.4	23.7	0.57	560	21	1.54	4.84
1.28	128	27	9.75	19.2	1.36	1360	49	0.33	1.05
13.1	1480	121	1.62	44.7	1.74	1740	47	1.62	7.24
194	57000	483	0.60	1.62	18.8	19200	157	0.0069	1.62

the precipitate ions enter into the composition. It is often difficult to resolve the question of the solution of precipitates under such conditions by theoretical calculations. This is explained by the variety of possible reactions between the ions composing the solutions and precipitate, and the variety of processes underlying precipitate solubility in each individual case.

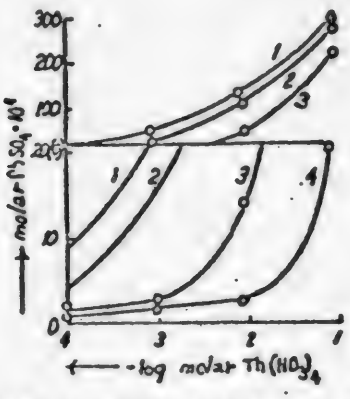

Fig. 1 - Solubility in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$ [Li_2SO_4]: 1 - 0.0 molar; 2 - 0.001 molar; 3 - 0.01 molar; 4 - 0.1 molar

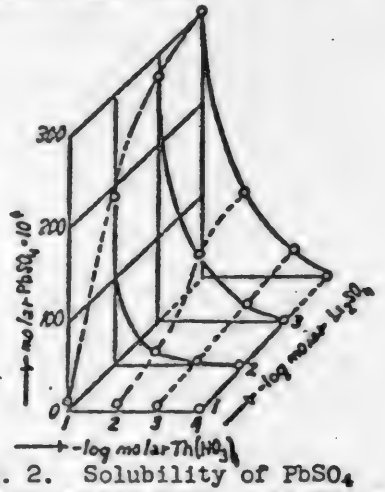

Fig. 2. Solubility of $PbSO_4$ in the system $PbSO_4 - Li_2SO_4 - Th(NO_3)_4 - H_2O$.

On the basis of literature results and of our own work on the study of precipitate solubility, we concluded that at the present time a universal method of calculating the solubility in complex systems is hardly feasible.

As shown previously and in the present work the calculation of precipitate solubility on the basis of the constant La is rendered difficult owing to the absence of results on the activity coefficient in complex systems. Calculation of activity coefficients according to the Debye-Huckel equation (second approximation), gives good results in many cases; however, in the presence of any appreciable chemical affinity in the system, this method becomes unsuitable.

As I. V. Tananaev and Deutchman [2] showed during the study of solubilities in the systems – metal fluorides (LiF, CaF_2, $PbFCl$) – $Be(NO_3)_2$ – H_2O, where chemical affinity is clearly manifested, that precipitate solubility can be calculated with a fairly good approximation to the true value, by the use of the values of the dissociation constants of the products formed in solution (in this case BeF^+) and of Lp in its usual form.

A similar conclusion was made above, in connection with the study of the solubility of $PbSO_4$ in the presence of $Th(NO_3)_4$ (formation of $ThSO_4^{2+}$).

An experiment in the application of physico-chemical analysis in the study of analytical systems containing precipitates showed us that these systems are usually considerably more complex than is normally assumed. Apart from the phenomena mentioned above, the precipitate itself very often changes its compositions owing to the formation of double (complex) salts, or solid solutions, so that any approach to the problem which does not take into account this aspect of the question, loses its justification and significance.

In spite of this, however, it seems that on the basis of the large amount of experimental data on the study of all possible forms of systems by the solubility method, it is possible at present to draw up a qualitative classification of systems containing precipitates, by means of which it will be possible to predict the direction of the process. For this purpose a diagram of the solubility of the precipitate in the presence of an electrolyte containing a common ion is used. This method was proposed by one of the authors [3] [1].

The diagram, represented by Fig. 3 illustrates the following types of systems. [2]

Type 1,1. Systems in which salting out of the precipitate (decrease in solubility) occurs on both the anion and cation sides. The effect of ions not common with precipitate ions is small. Complex formation is absent both on the anion and cation sides ($TlCl + Tl^+$; $TlCl + Cl^-$; $BaSO_4 + Ba^{2+}$; $BaSO_4 + SO_4^{2-}$).

Type 2,2. Partial salting out on the cation and anion sides with subsequent complex formation (increase in solubility) on both sides. The curves as a rule are unsymmetrical ($AgCl + Cl^-$; $AgCl + Ag^+$; $MgC_2O_4 + Mg^{2+}$; $MgC_2O_4 + C_2O_4^{2-}$).

Type 3,3. Strong complex formation on the cation and anion sides [$Th(C_2O_4)_2 + Th^{4+}$; $Th(C_2O_4)_2 + C_2O_4^{2-}$].

Type 1,2. Salting out and the absence of complex formation on the common cation side, and partial salting out with subsequent complex formation on the common anion side ($AgNO_2 + Ag^+$; $AgNO_2 + NO_2^-$).

Type 1,3. Salting out on the side of the cation, and strong complex formation on the anion side ($AgCN + Ag^+$; $AgCN + CN^-$).

Type 2,1. Partial salting out with subsequent complex formation on the side of the cation, and only salting out on the anion side ($MgF_2 + Mg^{2+}$; $MgF_2 + F^-$; $PbSO_4 + Pb^{2+}$; $PbSO_4 + SO_4^{2-}$).

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1) Reported by I. V. Tananaev at the meeting of the Scientific Council of the Institute of General and Inorganic Chemistry, Academy of Sciences USSR in 1943.

2) In these examples only the salt components of the system are indicated.

Type 2,3. Partial salting out with subsequent complex formation on the cation side, and strong complex formation on the anion side [$Al(OH)_3 + Al^{3+}$; $Al(OH)_3 + OH^-$].

Type 3,1. Strong complex formation on the cation side, and salting out on the anion side ($ThF_4 + Th^{4+}$; $ThF_4 + F^-$).

Type 3,2. Strong complex formation on the cation side, and partial salting out with subsequent complex formation on the anion side.

From the examples quoted above it is obvious that the curves can have the most diverse shapes, from curves having maxima (types 1,1; 1,2; 2,1) to curves having minima (type 3,3). Curves can also be obtained which do not intersect on the ordinate and correspond to the precipitate solubility in pure water (types 3,1 and 1,3). All this variety of curves is explained by the fact that the solubility of the precipitate is determined by processes which are mutually opposed, namely the salting out effect and complex formation. In this connection it is possible to imagine a limiting case where the solubility of the precipitate is expressed by a straight line parallel to the abscissa (the dotted line on Fig. 3), in such a case salting out and complex formation mutually compensate each other. Cases of pure salting out or complex formation respectively are rarely met. Salting out of $AlCl_3 \cdot 6H_2O$ or $BaCl_2$ by gaseous HCl is an example of the former, while the reaction $AgCN + CN \longrightarrow [AgCN]_2$ typifies the second.

The classification given above based to a considerable extent on the difference between systems, which arise from the ionic types of the individual components of these systems, indicates to a first approximation only part of the question of precipitate solubility. Fig. 3 represents such a system when the composition of the precipitate remains unchanged and corresponds to a simple salt. In the majority of cases however, changes occur in the precipitate as the result of various processes, in particular the formation of double salts or solid solutions. In such cases it is necessary to consider the whole diagram, in which every new phase is represented by the corresponding curve (branch) of solubilities.

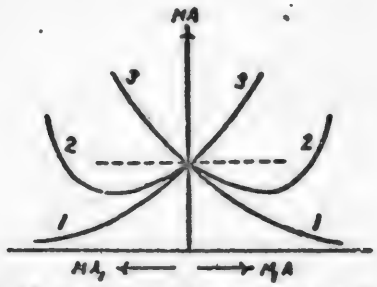

Fig. 3. Solubility of a salt (MA) in the presence of electrolytes with common ions (M,A and M_1A)

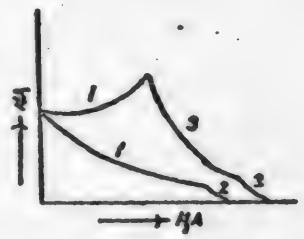

Fig. 4. Solubility of the precipitate (MA) in the presence of electrolyte (M_1A)
1 – MA; 2 – M_1A; 3 – $M_1[MA_2]$

The type of diagram which is obtained for the simplest case where one double salt occurs together with complex formation (on the anion side) is represented in Fig. 4. However, in many cases several new solid phases appear and the form of the diagram becomes correspondingly more complicated. A number of such cases are described in the literature. In particular the following systems may be mentioned: AlF_3–NaF–H_2O, in which $11NaF \cdot 4AlF_3$ and $AlF_3 \cdot 3NaF$ [4] separate out; FeF_3–KF–H_2O and AlF_3–KF–H_2O in which $FeF_3 \cdot 2KF \cdot H_2O$; $11KF \cdot 4FeF_3 \cdot 12H_2O$; $FeF_3 \cdot 3KF \cdot 3H_2O$; $AlF_3 \cdot 2KF \cdot H_2O$ and $AlF_3 \cdot 3KF$ can exist; [5,6]: $PbSO_4$–K_2SO_4–H_2O in which $PbSO_4$ and $PbSO_4 \cdot K_2SO_4$ separate out [7]: of particular interest in this connec-

tion are systems which contain insoluble ferrocyanides. Thus in the system $CoSO_4$-$K_4Fe(CN)_6$-H_2O, $5Co_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ and $4Co_2Fe(CN)_6 \cdot 3K_4Fe(CN)_6$ separate out [8]· in the system $CoSO_4$-$Na_4Fe(CN)_6$-H_2O the following are formed $Co_2Fe(CN)_6$; $10Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$; $3Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$ and $2Co_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$ [9]; in the system $CdSO_4$-$K_4Fe(CN)_6$-H_2O the compounds $5Cd_2Fe(CN)_6 \cdot 4K_4Fe(CN)_6$ and $Cd_2Fe(CN)_6 \cdot K_4Fe(CN)_6$ [10] are formed.

These examples of systems containing fluorides and ferrocyanides (which are not exceptions) show that systems containing precipitates can be very complex. Thus, in a number of the above systems, solid solutions were found as well as the slightly soluble double salts [1,11]. It is possible that in systems consisting of multivalent ions, hydrolysis also occurs with the formation of basic salts of different composition. This last possibility which leads to a complication of the picture as a whole, is not usually taken into consideration for the sake of further simplifications which are not always justified.

In the present article it is not proposed to give an exhaustive list of systems, in which a complex picture of the precipitation process is observed. This question is touched upon in the article of I. V. Tananaev already cited [3].

The aim of the present article, of necessity short, is to show that it is difficult to apply either one method or another of calculating the solubility of precipitates by means of Lp or Ls, to many analytical systems of practical importance which contain precipitates.

Table 2

Solubility of CaF_2 in the system CaF_2-$Al(NO_3)_3$-H_2O at 25°C.

$Al(NO_3)_3$ molar	$[Ca^{2+}]$ molar in satd. solution	$\frac{[F^-]\ total}{[Al(NO_3)_3]}$ in satd. solution	$K_{AlF_2^+} \cdot 10^+$
0.3	0.0524	0.35	2.34
0.1	0.0317	0.63	2.10
0.01	0.00681	1.36	2.40
0.003	0.00244	1.63	2.94
0.001	0.00096	1.92	1.38

In many cases the details of which forms of a particular compound exist in the solid phase and in solution are still uncertain. Details of the interactions between these various forms are also unknown. A typical example is the hitherto little studied formation of soluble, positively charged, predominately multivalent, metal ions containing unsaturated acido groups (left part of the diagram in Fig. 3. As we have shown previously [1] and in the present article, the solubility of a precipitate in such cases can be calculated on the basis of the dissociation constants of the slightly dissociated compounds formed in solution. This can be illustrated by taking as an example, the solubility in the system CaF_2-$Al(NO_3)_3$-H_2O, in which clearly defined interaction occurs according to the reaction [3].

$$Al^{3+} + 2F^- \longrightarrow AlF_2^+.$$

Results on the solubility of CaF_2 in solutions of $Al(NO_3)_3$ of different concentrations are given in Table 2.

The dissociation constants of AlF_2^+ can be calculated from the formula:

$$K_{AlF_2^+} = \frac{(Al^{3+}) \cdot (F^-)^2}{(AlF_2^+)} = \frac{[C_{Al(NO_3)_3} - (Ca^{2+})] \cdot \frac{L_{CaF_2}}{(Ca^{2+})}}{(Ca^{2+})}$$

It can be seen from Table 2 that the value of $K_{AlF_2^+}$ varies within the very narrow limits of $1.38 \cdot 10^{-9}$ to $2.94 \cdot 10^{-9}$ i.e. it is practically constant, although the concentration of $Al(NO_3)_3$ changes by 300 times.

It follows from this that the calculation of the solubility of a precipitate in the presence of a clearly manifest chemical affinity in the system, on the basis of the constancy of Lp, is possible with a fair approximation to the true value. In order to do this however, it is essential to have a clear idea of the composition of the compounds formed in solution.

What has been said in this review may be summarized as follows.

The problem of the solubility of precipitates in many practical systems, usually of complex composition, cannot be resolved at the present time on the basis of calculation, without recourse to all sorts of simplifications, and accepting the system as such and accepting changes in concentration of the components within wide limits and changes in the compositions of the precipitate (formation of double salts, solid solutions,etc.). The fullest information about the behavior of systems containing precipitates can be obtained by the study of systems containing precipitates by means of the physico-chemical analytical method, with careful characterization of the composition of the solid and liquid phases. The most important reaction for practical systems is the exchange decomposition of the general type:

$$MeA + M_1A_1 \rightleftharpoons \underset{\text{precipitate}}{MeA_1} + M_1A$$

in which ions common to and different from the precipitate ions participate.

At the present time experimental results on the study of such reactions are extremely few and work along these lines should be regarded as one of the most pressing problems of analytical chemistry. Only on the basis of such work, in which investigation of the solubility of systems is carried out simultaneously with careful study of the chemical affinity of solutions by means of physico-chemical analysis, can a rational theory of precipitation reactions be developed in future, not to mention diagrams of solubility, in particular three dimensional diagrams which make it possible to choose, without any errors, the method of precipitation in analytical practice.

SUMMARY

Solubility in the system $PbSO_4$–$Th(NO_3)_3$–Li_2SO_4–H_2O at 25° has been studied. It has been shown that the Debye-Huckel equation cannot be used for calculating the solubility of $PbSO_4$ in this system, owing to a clearly manifested chemical interaction which is accompanied apparently by the formation of complex ions of the type $ThSO_4^{2+}$.

Some ideas have been put forward regarding the significance of physico-chemical analysis for the theory and practice of precipitation reactions, in connection with which a diagram is given of the type of ternary system: precipitate-electrolyte with common ion-water, which embraces all possible systems containing precipitates, in relation to the ionic type of the components and the character of the interaction process in the system.

LITERATURE CITED

[1] I. V. Tananaev and I. B. Mizetskaya, J. Anal. Chem. 1, 6 (1946); 1, 94 (1946); 6, 337 (1951); Bull. Acad. Sci., Div. Chem. Sci. 4, 391 (1948).

[2] I. V. Tananaev and E. N. Deutchman, Bull. Acad. Sci.; Section Chem. Sci. 2, 144 (1949).

[3] I. V. Tananaev, Bull. Sect. Phys. Chem. Anal. 20, 277 (1950).

[4] I. V. Tananaev and Yu. L. Lelchuk, J. Anal. Chem. 2, 93 (1947).

[5] I. V. Tananaev and E. N. Deutchman, Bull. Acad. Sci. Div. Chem. Sci., 4, 373 (1946).

[6] I. V. Tananaev and M. A. Nekhamkina, Bull. Sect. Phys. Chem. Anal. 20, 227 (1950).

[7] I. V. Tananaev and I. B. Mizetskaya, Factory Lab., 6, 529, (1946).

[8] I. V. Tananaev and M. I. Levina, J. Anal. Chem. 3, 31 (1948).

[9] I. V. Tananaev and M. I. Levina, Factory Lab., 8, 887 (1949).

[10] I. V. Tananaev and A. S. Kozlov, J. Anal. Chem. 6, 149 (1951).

[11] I. V. Tananaev and M. I. Levina, J. Anal. Chem. 1, 224 (1946).

THE COMPLEX STUDY OF PRECIPITATES[1)]

A. V. Nikolaev and M. P. Elentukh

The formation of precipitates is a process which has been well known for a long time. Preparative and analytical chemistry, and factory practice have widely used difficultly soluble compounds. It is natural that a large amount of work has been devoted to this question, and many practical methods proposed, etc. Information on precipitates is to be found, e.g. in Kolthoff and Sandel's book on quantitative analysis [1].

The most common defect of many studies in this field is the absence of numerical values characterizing the precipitates themselves.

We have used a simple determination of the filtration coefficient, and studied a number of precipitates according to this and certain other properties [2]. We have made an attempt below to generalize the results obtained, using gypsum, and the hydroxides of magnesium iron and aluminum as examples.

Small crystals have the greatest solubility [1]; the velocity of solution depends on the difference between the actual concentration c'_2 of the precipitate in solution and the equilibrium concentration c'_1 in saturated solution of the precipitate.

If the difference $c'_2 - c'_1$ is large, then other conditions being equal, the solution velocity will be considerable and the small crystals will dissolve quickly while the coarse ones grow. On the other hand, a small value for $c'_2 - c'_1$ leads to a proportionate slowing down of this transfer, and leads ultimately to a continuous state of unbalance between fine and coarse particles.

During the separation of crystals from solution the difference $c_1 - c_2$ has an important effect, this is called the supersaturation and is the difference between the actual concentration c_1 of a given ion and the solubility of the precipitate c_2 coming out of solution. The greater the supersaturation, the higher the velocity with which the precipitate separates and the smaller the crystals formed. This is confirmed by many examples, in particular by Veimarn's work. It should be remembered that as precipitation proceeds c_1 falls and c_2 increases owing to the decrease in concentration of the original compound which has an ion in common with the precipitate. Obviously right at the end of precipitation (last drop) c_1 has for given conditions a minimum and c_2 a maximum numerical value respectively, i.e. the supersaturation $c_1 - c_2$ is a minimum.

The following methods can be used in order to attain minimum supersaturation for all precipitation processes: 1) decreasing c_1 (the use of dilute original solutions); 2) increasing c_2 to the maximum possible value (increasing the precipitate solubility); 3) decreasing c_1 and c_2 by the maintenance of conditions similar to those obtained during the addition of the last drop.

We shall briefly consider the effect of these methods on the precipitate.

1. A decrease in the concentration of both reagents can reduce the supersaturation many times over, and affect the distribution of particle size i.e. the quality of the precipitate. e.g. according to Veimarn's results, on the addition of 0.001 N solutions of a sulfate to a barium salt of the same concentration, the precipitate of $BaSO_4$ appears after 5 minutes, the solution being clear up to that time. Precipitation lasts 2 hours and the particle size is 5μ.

[1)] Report read at the Conference on Classical Methods of Chemical Analysis held in Moscow, Nov. 14-17, 1951.

For a concentration of the reactants of 0.0002 N, the precipitate takes a month to form and the particle size is 30 x 15μ. Obviously this method is of no practical interest on account of the large volume of reactants and the slowness of the process.

2. The effect of increasing the solubility of the precipitate is also well known, e.g. in order to get coarse crystals of $Mg(OH)_2$, precipitation is carried out in the presence of NH_4Cl or sugar; good crystals of AgCl can be obtained by evaporation of an ammoniacal solution of this compound; calcium oxalate is precipitated from acid solution etc. Factory practice uses relatively concentrated solutions of sodium aluminate, which is spontaneously precipitated with separation of aluminum hydroxide (centrifuge method). Hoffer [3] on the basis of a study of the particle size of precipitates, gave an empirical equation $M = AL^2$, where M is the particle size of the precipitate, A is a constant and L is the solubility of the given compound, which is applicable to both easily soluble and difficultly soluble compounds. This equation only holds for comparable conditions of precipitate formation, in particular for the time of preparation.

3. The last drop method (Method A), is easily attained in practice by the addition of the two reactants dropwise, and separately, to a definite volume of water or other solution (buffer) [2].

It is important that as each drop of one reactant is added to the buffer it is thoroughly distributed before a drop of the other reactant is added. It is obvious that this technique requires careful regulation of the time of addition. By decreasing the volume of the drops added and increasing the volume of buffer, it is possible theoretically to get any given degree of supersaturation. This is a very effective method, because by means of such a method it is possible to organize a continuous process of precipitation and to pour very concentrated solutions into the buffer (see below).

In addition to the last drop method (Method A) the supersaturation may be decreased by adding dropwise a solution of the precipitant to the solution to be precipitated (Method B). This method is widely used in laboratory practice. In both Method B and to a lesser extent in Method A, it is true that it is impossible to avoid local supersaturation at the point of entry of the drop into solution and during its distribution in the volume of liquid as a whole. Therefore the method of homogenous precipitation is worthy of consideration. The conditions for this method are the presence of precipitant and the expected precipitate in one phase (in solution), and the precipitation occurs as the result of a slow reaction. Examples of homogenous precipitation are the well known nitride method of precipitating iron and aluminum, and also Willari's method of precipitating calcium oxalate [1] in which ammonia released by the hydrolysis of urea $CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3$, neutralizes the acid.

Because of the small concentration of the gas, this form of precipitant is very successful, because only slight supersaturation occurs. We shall consider this method below using the carbonization of aluminate solutions as an example.

Among other factors it is necessary to consider the effect of temperature on precipitates. Since the majority of precipitates have a positive temperature coefficient of solubility, heating increases the solubility, and usually the quality of the precipitate is thereby favorably affected. It is easy to see that the action of heat can also be unfavorable (decrease of solubility with temperature).

Vant-Hoff [4] in his study of borates established that it is easier to obtain them in a crystalline form in porcelain rather than in glass vessels; he also established that in a series of cases the introduction of seed(crystals) shows an effect only when a large amount of them are used. In such a case it is

necessary to introduce the concept of surface action.

Spiro [5] independently established and used the favorable action of large amount of precipitate for the formation of new lots of precipitate. He called this method the accumulation method, because the first portion of precipitate which is formed, is used as a nucleus for the formation of a second portion of precipitate; these two portions then act as nuclei for a third, etc., i.e. the precipitate gradually accumulates on the first crystals. We verified the effectiveness of this method [2]. It should be noted here that the method mentioned above -Method A- (the last drop method), obviously uses all the precipitate obtained as nuclei, as many times as new portions of precipitant (drops) are added, for the whole process. A mathematical treatment of this question[1] (A. V. Nikolaev) gave the following number of contacts of the seed crystals with the precipitation zone during the whole period of precipitate formation.

1) Drop Method B: $ma\,[\ln(m + 1) - 1]$.

2) Drop Method A (without seed crystals) $\frac{(m - 2)ma}{2}$

3) Drop Method A (with seed crystals): m^2a.

4) n-th successive precipitation: $nma\,\ln(m + 1) - ma$.

5) for n successive accumulations: $\frac{n^2}{2}\,ma\,\ln(m + 1) - nma$, where a is the number of crystals formed from one portion (drop); n is the number of precipitations; m is the number of drops (portions).

Comparison of drop methods A and B shows that A gives a $250\left(\frac{2}{1}\right) - 500\left(\frac{3}{1}\right)$ times more efficient use of the seed crystals than B. Comparison of the accumulation method [5] and Method A shows that one precipitation according to Method A is equivalent to 20-30 precipitations by Spiro's method.

Thus Method A is interesting not only as a means of lowering supersaturation but also as a very effective method of using seed crystals for further precipitation.[2]

In concluding this part of the work it is necessary to consider some simple ideas from the colloid field, which we shall use later on. Particles of precipitate can grow larger (or flocculate) at the expense of the true growth of the crystal and can " stick together" to coagulate. Ordinary coagulants (heat and coagulators) can therefore lead to an enlargement of the particle, although as known previously each increase in particle size does not necessarily lead to an improvement in the precipitate [1].

It is also obvious that a precipitant can also act as a peptizing agent for the precipitant with all the consequences that that entails. (increase in the volume of the precipitate, a large final layer of deposit, etc.).

All the possible factors which can influence the quality of the precipitate, can act either with or against each other, e.g. in the majority of cases where heat is used, together with Method A, the effect of each factor is increased

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1) Only the final results are given due to economy of space.

2) We deem it a pleasant duty to record that Prof. N. A. Tananaev in his textbook of gravimetric analysis, proposed the method of pouring the two reactants into a buffer, before us. We arrived at this method independently of Tananaev's work and introduced some improvements - the use of seed crystals and the establishment of the minimum addition time.

separately. The method of homogenous precipitation usually matches with increase in precipitate solubility and with heating.

We have shown below by the use of four examples quoted previously, the effect of each of these factors, which enable us to define a more interesting field for further work. The filtration coefficient of the precipitate was taken as a criterion, i.e. the velocity in cm/sec of the movement of water in the precipitate for a gradient equal to unity.[1] The method of determination of the filtration coefficient has been described previously [2], accordingly it is not dealt with further. Only a diagram of the apparatus is adduced. (Fig.1). We obtained good reproducibility for the results as can be seen from the results of repeated determinations of the filtration coefficient K for three precipitates of $Fe(OH)_3$; I – 1.32; 1.14; 1.14; II – 1.7; 1.32; 1.32; III – 6.26; 6.34; 6.20. $K = 10^{-6}$ cm/sec.

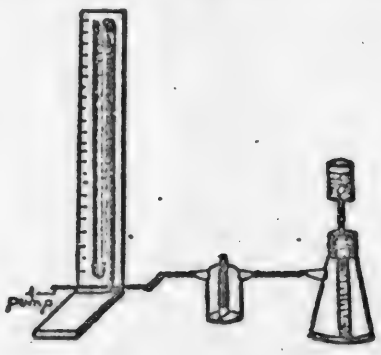

Fig. 1. Filtration apparatus

For I and II it was observed that the precipitate becomes gradually denser on the filter. It is not difficult to show theoretically that there is an inverse relation between the filtration coefficient and the square of the surface area of the precipitate particles (see e.g. [9]).

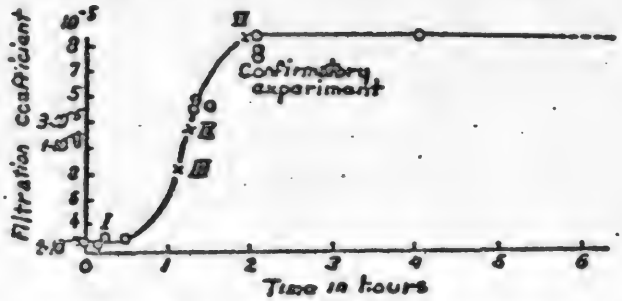

Fig. 2. Diagram of filtration of precipitates of $Mg(OH)_2$
×○– solutions of $MgSO_4$ and NaOH; ●– solutions $MgCl_2$ and $Ca(OH)_2$

We shall begin with Method B. The velocity of entry of precipitant drops can be greater than the velocity with which the drops are dispersed in the bulk of the solution. This leads to local supersaturation (from the meeting of the precipitation zone of the two drops) and to a depression of the growth of the particles. On decreasing the rate of addition a point is reached at which each drop will enter the solution just when the previous drop has been completely used up, the quality of the precipitate should then improve rapidly. Obviously further increases in the time of addition will not improve conditions much more than the critical rate. Results are given in Tables 1 and 2 below.

As can be seen from Table 1 and Fig. 2, our expectations were fully justified; for $Mg(OH)_2$ there are three groups and the increase in filtrability

1) Just as useful as a qualitative numerical character of precipitate and deposit is its dynamics of settling and the depth of the final layer on standing. See below and also [2].

is stepwise. The addition time acts favorably on gypsum precipitates, but has considerably less effect on such colloidal and difficultly soluble precipitates as $Fe(OH)_3$ and $Al(OH)_3$. True, for a 4 hour addition in Series 3 the filtration coefficient increases by 2-3 times; but this, of course cannot be compared with $Mg(OH)_2$, where K increases 40-100 times.

The effect of increasing the temperature has been studied in detail for $Fe(OH)_3$ and $Al(OH)_3$, i.e., for precipitates on which addition time does not have much effect. Results are given in Table 2.

TABLE 1

Filtration Velocity of Precipitates (10^{-7} cm/sec) fn Relation to Addition Time (precipitant dropwise)

No.	Precipitates	Addition time in hours						
		0.25	0.5	1	1.5	2.0	4.0	7.0
1	$Mg(OH)_2$; 10% solutions $MgSO_4$ and NaOH	Filtration coefficients 2.8	2.9	24.9	34.9	82-105	86-130	342
2	$Fe(OH)_3$; 5% solutions $FeCl_3$ and NaOH	11.8	15.0	-	14.0	11.6-13.2	-	-
3	$Fe(OH)_3$; 10% solutions $FeCl_3$ and NaOH	17.2	22.3	-	22.7	12-18.9	46.5-55	-
4	$Al(OH)_3$; 10% solutions $AlCl_3$ and NaOH	6-16.6	18.0	-	9.2-19.6	6.6-13.4	17.0	-
5	$Al(OH)_3$; 5% solutions $AlCl_3$ and NaOH	6	-	-	6.0	7.2	-	-
6	$CaSO_4 \cdot 2H_2O$; 10% solutions $CaCl_2$ and H_2SO_4	380-830	620-650	-	-	-	1300 - 1500 [1]	-

[1]) Addition time - 3 hours.

For addition times of less than 2 hours (1 drop/2 sec) the effect of temperature is not very significant for either $Al(OH)_3$, or for $Fe(OH)_3$ in particular (Compare with Table 1, Nos. 2 and 4). But since slow rates of addition are seldom used in practice, then it must be acknowledged that the action of heat alone is apparently exaggerated. This was unexpected, being contrary to general opinion, and so we repeated the experiments several times. Nevertheless, the results obtained were still the same. It is curious that heating has only a relatively small effect (increasing by 2-4 times) even for a 4-hour addition time (see No. 4, Table 1 and No. 3, Table 2); this is true also for a seven hour addition period.

Spiro's accumulation method which was tested for $Mg(OH)_2$ in particular, (see [2]) did not give better results even for 18 accumulations, than Method B for long addition times; this can be seen from Fig. 2, in which the Roman numerals represent the points for precipitates I-IX formed by accumulations. The accumulation method was therefore not used further.

The last drop Method A, obviously is effective only for a definite addition rate; thus, the precipitate of $Mg(OH)_2$ for an addition time of 15 minutes to the buffer cannot be filtered; for a 48-minute addition period K = $7.5\text{-}11.0 \cdot 10^{-6}$ cm per second, and for a 2 hour addition period K = $1.0 \cdot 10^{-5}$ cm/sec. No better results were obtained with this method than with Method B, but the advantages of Method A become apparent when $Ca(OH)_2$ is used instead of NaOH; it was only by means of Method A that a precipitate could be prepared with a K = 10^{-5} cm/sec, when

$Ca(OH)_2$ was used as the precipitant. For $Al(OH)_3$, the precipitates obtained had a filtration coefficient of $8-9 \cdot 10^{-8}$ cm/sec for addition times of 1.5-3 hours, but these precipitates had one very important advantage - they settled out incomparably better than those obtained by Method B.

Table 2

Relation between Filtration Coefficients (K) of Precipitates (10^{-7} cm/sec) and the Addition Time at 80-90°C

No.	Precipitate	Addition Time in Hours					
		0.25	0.5	1.5	2.0	4.0	7.0
1	$Fe(OH)_3$; 5% solns. $FeCl_3$ and NaOH	12-19	-	13	13.4	1)	-
2	$Al(OH)_3$; 5% solns. $AlCl_3$ and NaOH (alkali to Al salt)	7.8	11.0	18.4	15.6	-	-
3	$Al(OH)_3$; 10% solns. $AlCl_3$ and NaOH (Al salt to alkali)	-	-	-	14.1-17.7	35-48	85-97

1) Long experiments in the precipitation of $Fe(OH)_3$ with heating give very badly filtering precipitates owing to changes in the precipitate.

$Fe(OH)_3$ precipitates obtained by Method A have a maximum filtration coefficient of $6.2 \cdot 10^{-8}$ cm/sec for a 2 hour addition time; these precipitates which settled out considerably better than precipitates obtained by other methods, were friable in appearance and did not smear glass.

By means of Method A precipitates of $CaSO_4$ were obtained for a 1 hour addition period with 96% H_2SO_4 as precipitant, which had record values for the filtration coefficient ($3.3-3.7 \cdot 10^{-4}$ cm/sec[2]). It is important to observe that even when 10% H_2SO_4 was used in Method B, the precipitates obtained did not have filtration coefficients better than $K = 5-6 \cdot 10^{-5}$ cm/sec. Thus Method A is very effective for some precipitates.

The method of homogenous precipitation was tested on $Fe(CH)_3$ (nitride method). The precipitate obtained had a $K = 3.5 \cdot 10^{-8}$ cm/sec, i.e. better than the normal iron precipitates, in addition it settled out very rapidly as can be seen from Table 3.

Only typical crystalline precipitates settled out as quickly.

In the carbonization of aluminate solutions we come across a case of the action of a gaseous precipitant. The result obtained was unique because in addition to a small supersaturation on addition of the precipitant, the solubility of the precipitate is comparatively good. The corresponding results are given in Table 4.

The significant effect of elevating the temperature is very curious in this case. The filtration coefficient was determined for a sample of factory produced $Al(OH)_3$ prepared by the centrifuge method (the precipitate was given to us by Prof. A. I. Lainder to whom we extend our thanks) and was found to be equal to $2.75 \cdot 10^{-4}$ cm/sec, i.e. somewhat worse than $Al(OH)_3$ obtained by the carbonization method.

2) In speed of filtration these precipitates are comparable with coarse grain sand.

Table 3

Settling Velocity of Precipitates of $Fe(OH)_3$; Obtained by the Nitride Method
(total layer: solid + liquid = 4.0 cm)

	Settling Time						
	10 min.	20 min.	30 min.	1 hour	2 hours	3 hours	3.5 hours
Precipitate layer in cm	0.8	0.75	0.75	0.75	0.75	0.75	0.75

NOTE: Final ratio $\frac{\text{solid}}{\text{liquid}} = 0.23$.

Results are given below which were obtained for $CaSO_4$ by means of Method B, and which illustrate the effect of the precipitant cation. In all cases 10% solutions of $CaCl_2$ were used, and 10% solutions of H_2SO_4, $MgSO_4$, Na_2SO_4, and K_2SO_4 used as precipitants.

Table 4

Carbonization of a 10% soln. in hours	Temp., °C	Filtration Coeff. K in cm/sec
4	Room	$8.7 \cdot 10^{-5}$
4	90-100	$3.0 \cdot 10^{-4}$
4	90-100	$6.0 \cdot 10^{-4}$

Record results were obtained for Na_2SO_4 and K_2SO_4.[1] These good results for instantaneous addition are apparently connected with the following interesting observations. After mixing in the course of a few tens of seconds, or often up to one minute, the solution obtained remained clear, and only at the end of that time did crystallization commence. The preparative process, which occurs in the supersaturated solution, apparently facilitates subsequent crystallization.

Table 5

Filtration Coefficients for $CaSO_4$ Precipitates
(10^{-7} cm/sec)

Precipitant (10% solutions)	Addition Time in Hours		
	instantaneously	1.0	3
H_2SO_4	680-1100	620-650	1300-1500
$MgSO_4$	520	440	1200
Na_2SO_4	2300	2000	2500
K_2SO_4	2100	3600	3100

The effect of coagulators was investigated for $Fe(OH)_3$ and $Al(OH)_3$, they were added so as to give a 5% solution. The concentration of the solution of iron and aluminum salts and the NaOH was also 5%.

It can be seen from Table 6 that coagulators increase the filtration coefficient of $Al(OH)_3$ by 4-15 times; on heating the solution, the sulfate coagulators give even higher results, but the action of chloride coagulators, in almost all cases, was unaffected by temperature and in some cases their action was even impaired. From Table 6 in particular it follows that in the analytical determination of aluminum, in order to improve the precipitate quality, it is better to precipitate the $Al(OH)_3$ in the presence of ammonium sulfate than the chloride which is the one usually used.

1) The intermediate formation of fairly soluble double compounds of the type of glauberite or syngenite could be postulated here.

Ammonium chloride increased the filtration coefficient of $Fe(OH)_3$ in the cold 3-4 times, but Na_2SO_4 did not have any effect [contrast to $Al(OH)_3$]. On heating, both ammonium chloride and Na_2SO_4 increased the filtration coefficient. In this case, therefore, the use of ammonium chloride in the analytical precipitation of $Fe(OH)_3$ is justified.

Table 6

Filtration Coefficients of Precipitates (10^{-7} cm/sec) $Al(OH)_3$ and $Fe(OH)_3$ on addition of coagulators (5%)

Addition time [1 drop/2 sec]

Precipitate	Coagulators					Observations
	NaCl	NH_4Cl	$CaCl_2$	Na_2SO_4	$(NH_4)_2SO_4$	
$Al(OH)_3$	20-25	44.8	32.4	67.5-74.2	87.6	Ppt. obtained in the cold
$Al(OH)_3$	8.1	14.2	6.3	74-133	98.4	Ppt. obtained at 80°
$Fe(OH)_3$	12.1	54.3	9.5	13-20	-	Ppt. obtained in the cold
$Fe(OH)_3$	14.7	53.1	13.0	31.2	-	Ppt. obtained at 80°

Experiments were carried out on the precipitation of $Fe(OH)_3$ in which NH_3 and Na_2CO_3 were used instead of NaOH. [Rate of addition 1 drop/2 sec]. The filtration coefficient for NH_3 was $K = 1.77 \cdot 10^{-6}$ cm/sec while for Na_2CO_3 $K = 2.6 \cdot 10^{-6}$ cm/sec, whether the precipitation was carried out in the cold or at 70-80°, thus Na_2CO_3 gives a slightly better precipitate; it settles out quite well (see Table 10).

It is interesting that the substitution of $Ca(OH)_2$ for NaOH in the precipitation of $Mg(OH)_2$ gave an easily filterable precipitate only by the last drop Method A (1 drop/2 sec); but these precipitates settle out badly (particle adhesion).

The better filtrability of $Al(OH)_3$ and $Fe(OH)_3$ for the 10% series as compared with the 5% series is the result of a coagulating effect of this kind; the coagulant NaCl is formed during the reaction. Special experiments were made for $Mg(OH)_2$ in which 31.8% NaOH and 23% $MgSO_4$ were used, and in spite of a $1\frac{1}{2}$ hour addition time, the precipitate obtained had a $K = 8 \cdot 10^{-7}$ cm/sec (poor filtration). In this case the coagulating effect is negative and stops the true crystal growth. Thus N. A. Tananaev's rule is confirmed for $Fe(OH)_3$ and $Al(OH)_3$ but not for $Mg(OH)_2$.

When the colorimetric method of determining lithium is applied to natural brine with a 25-30% salt concentration the problem of separating magnesium as the hydroxide crops up. The application of Method A with $Ba(OH)_2$ as precipitant and the use of heat yields a precipitate with $K = 2.5\text{-}3.6 \cdot 10^{-6}$ cm/sec, which settles readily (see 8, Table 10). The coagulating effect here could not be completely suppressed which testifies to a definite limitation of Tananaev's rule.

The peptizing action of alkali together with a decrease in the solubility of hydroxide precipitates should become apparent when an inverse order of addition is used, e.g. adding a magnesium salt to alkali; in spite of a 2 hour addition time for 10% solutions the precipitate formed had a $K = 5 \cdot 10^{-7}$ cm/sec i.e. a twentieth of that for the normal method of addition. Consequently it is

to be expected that a lower result should be obtained for $Fe(OH)_3$ also. This was however, not confirmed experimentally, thus 5% solutions for a 2 hour addition time gave a precipitate for which $K = 1.32 \cdot 10^{-6}$ and 10% solutions gave precipitates with K = 1.2 and $1.9 \cdot 10^{-6}$ cm sec (compare Table 7).

Table 7

	Method B					Method A	Centri-fuging method	Carboni-zation of aluminate solutions
	Normal ppt. 5% series	Same for 10% series	Increase in temp. during addition of 15% solution	Increase in conc. and addition time	Coagula-tors and increase in temp.			
$K = 10^{-4}$ cm/sec	0.6	1.7	1.1	9.7[1]	10.5-13.3	8-9	275	301-663[2]
Number of times increased	1.0	2.4	1.9	16	18-22	13-15	460	500-1000

1) Inverse addition.
2) At 90-100°, in the cold $K = 8.7 \cdot 10^{-5}$, i.e. increases 145 times.

On the addition of aluminum salts to alkali to form $Al(OH)_3$ a solution of aluminate is initially formed which is then decomposed by the aluminum salt according to the equation:

$$3NaAlO_2 + 6H_2O + AlCl_3 \longrightarrow 4Al(OH)_3 + 3NaCl$$

This decomposition period was extended to 4 and 7 hours. In this way the results of the third series given in Table 2 were obtained. As can be seen the precipitate formed was 30 to 50 times more difficult to filter than when decomposition of the aluminate was effected by CO_2, but about ten times easier than usual precipitates.

In concluding this section it is interesting to record results on the filtration coefficients of $Al(OH)_3$ prepared by different methods.

Without entering into a detailed discussion of this table, it can be said that the simple methods usually used (e.g. Tables 4,5 and 6) improve the filtrability of a precipitate (13-22 times) but increase of solubility and introduction of the reactants with minimum local supersaturation (gas) give a qualitatively different effect (an increase in filtration by 500-1000 times). On the basis of this method, therefore, it is necessary to get similar good results for other precipitates. The difference in the phase composition of the precipitates should be noted (for aluminates - other hydrated forms of Al_2O_3).

In confirmation of this we shall turn our attention to the fact that such a relatively soluble compound as $CaSO_4$ (0.22%), even for poor samples of precipitate has a $K = 3.8 \cdot 10^{-5}$ cm/sec[3] while good samples have a $K = 7.6 \cdot 10^{-4}$ cm/sec. For $CaSO_4$ the upper limit is the same as for $Al(OH)_3$, although the solubility of $Al(OH)_3$ in the usual media is small.[4] Apart from the good solubility of $CaSO_4$, the form of the crystals which has a definite significance, ensures loose packing on the filter.

3) This value of K for $Mg(OH)_2$ is only attained for the best precipitates.
4) In view of the final solution after carbonization.

Because of the extended form of the crystals of $CaSO_4$ the precipitates settle out rather poorly.

The use of the amphoteric nature of $Al(OH)_3$ gave exceptional results as mentioned above; the method cannot be used for $Fe(OH)_3$ and we did not succeed in getting any better results by Method A than a precipitate with $K = 6.2 \cdot 10^{-6}$ cm/sec.[1] It is interesting to try and find conditions for the precipitation of $Fe(OH)_3$ similar to those for $Al(OH)_3$. The best and worst precipitates of $Fe(OH)_3$ differ by 6-8 times in their filtrability.

Success was achieved for $Mg(OH)_2$ apparently because of its large solubility (solubility product for $Mg(OH)_2 = 10^{-10}$); therefore in conditions of low supersaturation (long addition time, by the use of Method A etc.) good precipitates with $K = 3 \cdot 10^{-5}$ cm/sec were obtained. Results are given for K for four precipitates. In concluding this section we shall deal with a few general questions. Let us consider first whether particles of the precipitate grow or stick together. We succeeded in showing in the case of $CaSO_4$ and $Mg(OH)_2$ the existence of "secondary" coagulation of the adhesion type [2]. This was the result of the large emanating capacity of this type of precipitate [2] and the presence in the case of bad precipitates of coarser particles, when they were measured microscopically and by Figurovsky's method (sedimentation). But since precipitates with such "coarse" particles filter with difficulty, then it is natural to postulate an unstable adhesion of the particles, which the hydrostatic pressure during filtering can break down and thereby alter the form of the precipitate [2].

Table 8

Comparison of Filtration Coefficients for 4 Precipitates

Precipitate	$Mg(OH)_2$	$Fe(OH)_3$	$Al(OH)_3$	$CaSO_4 \cdot 2H_2O$
Solubility product or solubility in g/liter	10^{-10}	10^{-38}	10^{-38}	2.2
K_B Best ppts. in cm/sec	$3\text{-}4 \cdot 10^{-5}$	$6.2 \cdot 10^{-6}$	$7 \cdot 10^{-4}$	$7.6 \cdot 10^{-4}$
K_W Worst ppts. in cm/sec	$2.8 \cdot 10^{-7}$	$8 \cdot 10^{-7}$	$6 \cdot 10^{-7}$	$3.8 \cdot 10^{-5}$
$\frac{K_B}{K_W}$	>100	~8	>1000	20

This secondary coarsening was shown experimentally. In Fig. 3 are given diagrams for the particle distribution of $Mg(OH)_2$ for a 20 minute and $1\frac{1}{2}$ hour precipitation; it can be seen that the badly filtering precipitate (20 minutes) has the coarser crystals. Then a four hour addition period was tried under the usual conditions with addition of up to 20% NaCl (coagulant). Determination of particle size in this case showed an even greater trail of coarse particles, undoubtedly because of secondary coarsening. The filtrability of the precipitate was depressed as was to be expected.

Consideration of Figs. 3 and 4 shows that good precipitates are surprisingly homogenous with regard to particle size distribution, thus for a 3-hour precipitation, 70% of the particles had radii of 6-8μ.[2] It is obvious that on improvement

[1] It is curious that precipitates of $Fe(OH)_3$ obtained by the homogenous precipitation method filter even slightly worse.

[2] In the theory of the water permeability of soils it is shown, that the presence of 10% of small particles determines the filtration of the soil (reason given by Mendeleev, see [7], p. 81.

the precipitates become even more homogenous, i.e. there is a limit in particle growth for given conditions of adhesion [2]. The existence of this limit is confirmed by the horizontal trend of the upper part of curve in Fig. 2 and also by sedimentation curves and X-ray photographs. X-ray photographs also show that precipitates consist of real and not ideal crystals. The presence of forking on X-ray photographs for the lines of good precipitates indicates that there are large internal stresses in the crystals because of irregular growth on the different faces. Block-crystallization is the reason for the limiting growth of particles during adhesion [2]. Block-crystallization also determines the trapping of mother liquor by the precipitate, and can anew explain the phenomena of coprecipitation and trapping (see below).

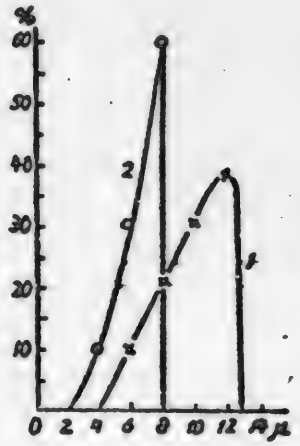

Fig. 3. Particle size distribution. Addition time: 1 – 20 min.; 2 – 1 hr. 30 min.

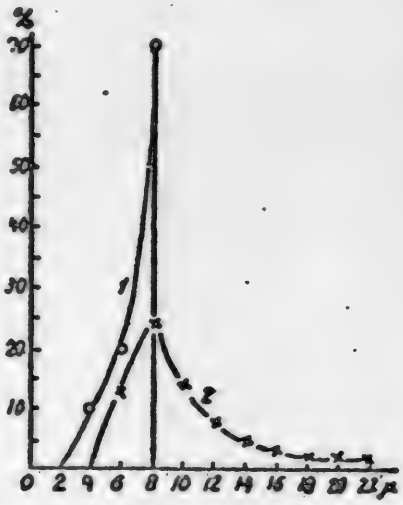

Fig. 4. Particle size distribution Addition time 3 hrs. 1) Without additive; 2) with addition of NaCl.

In addition to the particle size, their emanating capacity and the differences in the X-ray photographs of precipitates with different filtration coefficients, precipitates also differ in other respects. The heating and dehydration of precipitates of $Mg(OH)_2$ corresponding to the lower and upper parts of the curve in Fig. 2 are represented in Figs. 5 and 6. From Fig. 5 it can be seen that the cessation of boiling (decomposition of the hydroxide) for small precipitates can be 25° lower than for coarse precipitates. These two curves reproduce experimentally two types of brucite [the natural form of $Mg(OH)_2$], discovered earlier [8]. Thus conditions similar to those employed by us are also met in nature.

The break on the heating curve in the case considered corresponds to boiling, or more exactly, to the dissocation tension equal to 1 atmosphere. [$Mg(OH)_2 \longrightarrow MgO + H_2O$] It is obvious that dehydration under isothermal conditions should differ considerably; this is shown with great clarity in Fig. 6: where I is the precipitate containing small crystals which have been dehydrated in the course of a few days; VI and IX are precipitates (similar to the 2-hour one) which lose a similar amount of water only after 40 days and this at a temperature of 250°, and under exactly the same conditions (the same oven, the same weights and crucibles, etc.).

Some results for the washability of precipitates are given below. Precipitates of $Mg(OH)_2$ formed after 9 accumulations by Spiro's method and washed until no reaction for SO_4^{2-} was given by the wash liquors contained the following amounts of SO_4^{2-} in the precipitate (Table 9).

In a repeat of the 9 accumulations the last precipitate contained 0.25% SO_4^{2-}. A precipitate obtained by Method A for a 2 hour precipitation time (the best precipitate for filtrability) contained 0.40% SO_4^{2-}, while a precipitate obtained by inverse addition (worse precipitate for filtration) contained 0.13% SO_4. Factory precipitates of $Al(OH)_3$ are known to contain an appreciable amount of sodium which has not been washed out, with a consequent bad effect on the quality of metallic aluminum. It is also known from factory practice that when precipitates contain coarse crystals it is difficult to get a very pure product. Therefore in the preparation of analytical precipitates it follows that they can be obtained in an easily filterable state only by separation from the main bulk of the contaminating ions of the mother liquor, but precipitation of easily filterable precipitates before calcining, apparently cannot be recommended.

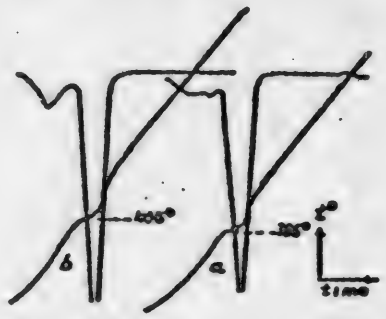

Fig. 5. Thermogram of $Mg(OH)_2$ ppts. Recording of both thermograms was made on one sheet of photographic paper.

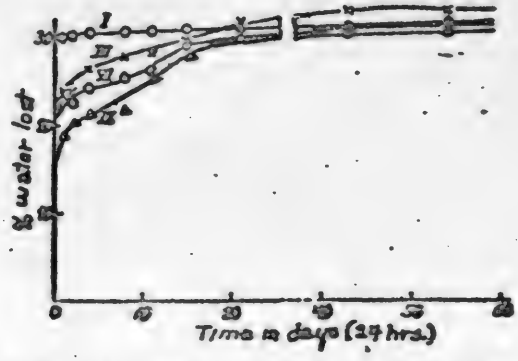

Fig. 6. Dehydration of precipitates of $Mg(OH)_2$ at 250°
Precipitates I-IX precipitated by the accumulation method

It is interesting that the usual adsorption mechanism for entrapping is not so responsible for the contamination of precipitates as is usually accepted. Thus, a precipitate which filters badly (I, Table 9) showed least contamination.

The curves for the settling rates of precipitates in general behave similarily to the filtration coefficient, as can be seen from Fig. 7 for $Mg(OH)_2$ precipitates. From curves 2-6 Fig. 7, the approach to a definite value is clearly shown both by the filtration coefficient, and the determination of particle size of the precipitates (see above). A case where the filtration coefficient did not correspond to the settling rate of the same precipitate was observed earlier, and is connected with unstable adhesion of the particles.

A very interesting phenomenon was observed during the precipitation of $Al(OH)_3$ and $Fe(OH)_3$ in 5 and 10% solutions. After addition of approximately 70-80% of the precipitant, all the contents of the vessel transformed into a fairly thick gel, that often stopped the stirrer. However, on further dilution of the alkali, the gel thinned out and at the equivalent point gelatinization ceased. The presence of developing space links between the particles is manifested in a very interesting type of settling out. Initially there is no settling out at all (10-40 minutes), but then a very sudden and rapid onset of settling out commences.

Gelatinization was never observed with precipitates prepared by Method A, which indicates that the surface forces of the particles of this type of precipitate are saturated, e.g. $Fe(OH)_3$ obtained by this method, did not smear glass and was friable.

Finally Table 10 gives the values of the final settled out layer in cm for a total layer of 4 cm after mixing. All the results are for 10% solutions.

Table 9

No. Precipitates	I	III	IV	IX
% SO_4^{2-} in precipitates	0.05	0.15	0.14	0.17

NOTE. Since this is essentially a one accumulation precipitate, then obviously, the mechanism of intercrystalline entrapment acts.

Results for precipitates for which the final settling layer is attained in 10-15 minutes or less are given in square brackets; in the dotted square brackets results are given for precipitates, in which settling out finished in 20-30 minutes.

The amphoteric character of precipitates of $Fe(OH)_3$ is shown by the fact that the precipitates are friable. Packing of precipitates may be effected by use of Method A, by precipitation with Na_2CO_3, by the addition of a coagulant and especially by the homogenous precipitation method. In the last case packing of the precipitate was the same as for the remaining three precipitates which could almost never be prepared in an amorphous condition as estimated by X-ray photographs.

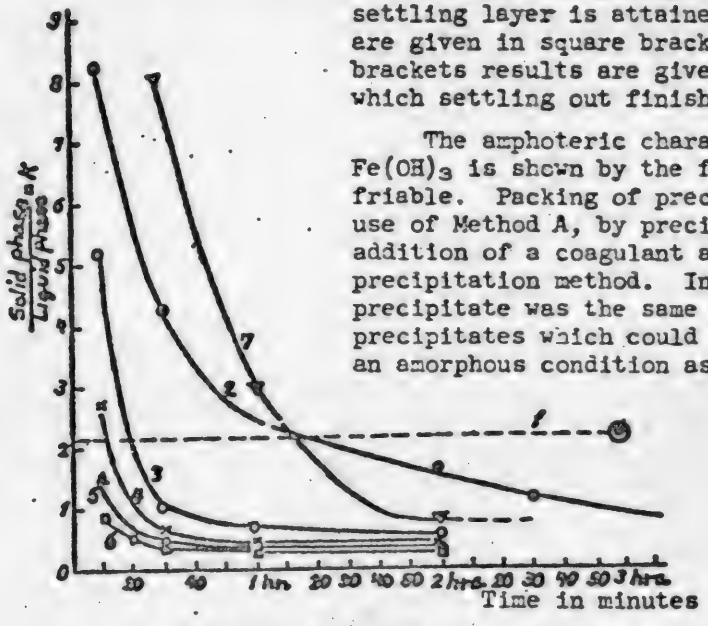

Fig. 7. Settling out of $Mg(OH)_2$ precipitates. Time of NaOH addition: 1 - 0.25 hr; 2 - 0.5 hr; 3 - 1 hr; 4 - 2 hrs.; 5 - 4 hrs.; 6 - 7 hrs.; 7 - confirmatory expt. (2 hrs)

For Method B packing was equal for $Mg(OH)_2$ and $Al(OH)_3$. For an inverse method of addition, the precipitates of $Mg(OH)_2$ and $Fe(OH)_3$ showed a breaking up from the OH-ion ; while for $Al(OH)_3$ the precipitate obtained was denser in complete agreement with its amphoteric character.

TABLE 10

Time and Method of Preparing Precipitates

Precipitate	Method B: time in hours				Reverse drop 2 hours	Method A		Nitride method	Carbonization of aluminate	Method B	
	0.25	0.5	1.5	2		without heating	with heating			Na_2CO_3 precipitant	Coagulant Na_2SO_4 with heating
$Mg(OH)_2$	1.8	1.5	1.2-1.3	1.2 (0.9[1])	3.3	1.4	1.0	-	-	-	-
$CaSO_4 \cdot 2H_2O$	3.3	-	0.75	0.7	-	0.7	0.7	-	-	-	-
$Al(OH)_3$	1.0	1.35-1.5	1.05	1.25	0.6	1.0	0.7	-	0.7	-	-
$Fe(OH)_3$	3.6	3.45	3.4	3.15	3.45	3.1	1.16	0.75	-	1.7	1.45

[1]) For 4-hour addition.

The best settling out was observed for $Mg(OH)_2$ for a 7-hour addition time by Method B, and by Method A with heating.

It is interesting that a layer less than 0.6-0.7 cm was not obtained for any precipitate (10% of the solution).

In conclusion it is necessary to emphasize once again that the measurement of such simple magnitudes as the filtration coefficient, the settling velocity, and thickness of the final settled layer gives very important and useful results about precipitates.

We intend to take this into account during further investigations, in which it will be possible to compare more than four precipitates.

LITERATURE CITED

[1] Kolthoff and Sandell, Quantitative Analysis, State Chemical Press, 1938.

[2] A.V.Nikolaev, J.Appl.Chem. 20, No. 3, 187 (1947); ibid 20, No. 7, 697 (1947).

[3] E. Hoffer, Z. phys. Chem., A 183, 455 (1939).

[4] Vant-Hoff, Oceanic Deposition of Salts, United Sci-Tech.Press, 1936

[5] N.S.Spiro, Bulletin All-Union Sci. Res. Inst. Haloids, Leningrad, 1939-40.

[6] T.Svedberg, Colloid Chemistry, State Technical Press, 1930, p. 56-58.

[7] Collected papers "Protective Films on Salts", Acad. Sci. Press, 1944, p.81.

[8] N.S.Kurnakov and V.V.Chernykh, Collected Works of N.S.Kurnakov, Vol. 1, Chem.Theory Press, Leningrad, 1938, p. 441.

[9] V.V.Tovarov, Factory Lab., No. 1, 1948, p. 68.

[10] A.V.Nikolaev and A.A.Sorokina, Proc. Acad. Sci., 77, No. 3, 427.

COMPLEX COMPOUNDS AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY[1)]

D. I. Ryabchikov

Vernadsky Inst. Geochem. and Anal. Chem. Acad. Sci., Moscow

For some time past in connection with increasing attention to control, particularly of new processes, the scope of investigations in analytical chemistry has not only widened, but the character of the investigations themselves has changed. This is reflected in attempts to depart from empirical and semi-empirical analytical methods and to work out methods which are based firmly on the basic principles of inorganic and physical chemistry.

In analytical chemistry the very attractive theory exists that it is possible to find ways of independently determining chemical elements in the presence of others. The new problem of determining and controlling so called traces and mixtures on the background of an excess of the main elements has arisen.

The development of methods for isolation, separation and estimation of many rare and widely scattered elements has become an independent problem.

Progress in analytical chemistry to a considerable degree develops along the path of the widest use in analytical chemistry of such instrumental methods of analysis as the photocolorimetric, electroanalytical, polarographic, spectrographic, X-ray, mass spectrographic, chromatographic, luminescent, and radiochemical methods, as well as the use of radioactive isotopes.

The use of instruments in analytical chemistry does not lessen, but in fact increases the tempo of investigation of chemical reaction in solutions.

If under these conditions the classical methods of analytical chemistry begin partly to loose their independent significance, on the other hand the accumulation of a vast amount of experiments on the relation of the chemical affinity of analytical processes constitutes a basis for the instrumental methods, the successful use of which often depends on the extent of the identification of the material to be determined.

In order to solve new problems in analytical chemistry both here and abroad more and more investigations are being carried out on the discovery and use of special organic compounds for use as precipitants, pigments and indicators. Many organic reagents are already firmly established in practical analysis because of the high intensity of the colors of the compounds formed and the low solubility of the precipitates.

The problems of analytical chemistry which are of practical importance can be successfully solved by a more fundamental approach to the chemical side of analytical processes by a more complete use of the fine structure of molecules created by the analyst.

Nevertheless in analytical chemistry there is still a definite neglect of the chemical side of processes, particularly in the more complicated cases connected with complex formation. If, as a rule, in all analytical processes the valency state of an element is taken into account, the coordination number of the instab-

[1)] Report read at the Conference on Classical Methods of Chemical Analysis, held in Moscow on November 14-17, 1951.

ility constants for many elements still remain unknown, and deliberate control of the chemical affinity of an analytical process is impossible without knowledge of the coordination possibilities, the dimensions of the ionic radii and charges, and the capacity of individual groups and molecular residues for complex formation.

Platinum and to a lesser degree some of the elements in the same group, is the only metal whose stereochemistry has been more or less studied in detail. The complex compounds of the majority of the other elements have either been studied unsystematically and superficially or have not been studied at all. It is sufficient to remember that the stereochemistry of such an ancient element as gold is still little known, to say nothing of many rare and scattered elements. The physical chemistry of even known complex compounds is in an even more unsatisfactory state. There are no conclusive experimental results on the instability of many complex compounds of importance in analytical chemistry, in aqueous solution in relation to pH and other factors. Numerical values of the instability constants of complex compounds of different elements are no less necessary for analytical chemistry today than the solubility product values. Thermal stability, decomposition potential, the phenomena of oxidation and reduction of complex compounds, and others have still not found wide application in analytical chemistry.

On examination of textbooks and specialist literature it is easy to be convinced that the formation of complex compounds is very widely used in analytical chemistry.

From the time of the discovery by Ilinsky of the reaction of Co with α-nitroso-β-naphthol [1] and afterwards of Ni and Pa with dimethylglyoxime by Chugaev [2], inner complex compounds have been widely used in practical analytical chemistry. Hydroxyquinone, rubeanic acid, thiourea, diethylthiocarbamate, diphenylthiocarbzone, and many other organic reagents, specially synthesized for analytical purposes, have often been applied in colorimetry for preparing colored complexes and for the precipitation of the elements.

Information on inner complex compounds of interest in analytical chemistry is given in Voznesensky's book [3]. Kuznetsov [4] has carried out systematic study in this field.

It must be noted that the study of the reactions of organic reagents, unfortunately is still of a predominantly qualitative nature. We often do not know even the composition of the reaction products and the chemical affinity of the process of formation and decomposition of intracomplex compounds.

Inner-complex compounds are of special interest for analytical chemistry and should be considered independently. Below we give examples of the application of some special complexes in analytical chemistry.

Of great importance in analytical practice are phenomena such as the so-called "masking", whereby with the help of complex forming compounds interference from similar elements can be eliminated. Thus the determination of rhodium in platinum-rhodium alloys (contact, thermopar) is exceptionally difficult. It has been shown that both metals behave differently towards sulfites [5]. Pt after dissolving in aqua regia, in aqueous solution is in the form of $[PtCl_6]^{2-}$ which is of an orange color while Rh as $[RhCl_6]^{3-}$ gives an intense rose color. On addition of Na_2SO_3 to the mixture the sulfite reacts only with Pt forming a completely colorless complex sulfite compound of the composition $Na_6[Pt(SO_3)_4]$. Rh remains unchanged and can be determined from the characteristic color of the chlororhodiate.

A small number of rare earth elements and Ca can be separated from Fe, by the addition of NH_4F to the solution which is being analyzed. Fe forms a stable soluble complex of the composition $(NH_4)_3[FeF_6]$, while the rare earths and Ca are

precipitated as fluorides.

Fe ions are bound into a stable complex by the addition of citrate, tartrate, phosphate, pyrophosphate etc., to form anions of the composition $[Fe(Cit)_2]^{3-}$, $[Fe(Tar)_3]^{3-}$, $[Fe(PO_4)_3]^{3-}$, $[Fe_2(P_2O_7)_3]^{6-}$ [6]. Fe cannot be detected in solutions containing such complex compounds even with the most sensitive reagents.

Zr can be transformed into a very stable citrate complex of the composition $H_4[ZrF_2Cit_2]$ in the determination of small amounts P in metallic Zr by ammonium molybdate.

In order to avoid interference from Fe, Ni, Co in the determination of Cu by rubeanic acid, citric acid is added [7]. The interfering metals are combined into very stable complex anions of the composition $[Me(Cit)_2]^{4-}$, while Cu in these conditions is reduced to the univalent state and yields a difficultly soluble rubeanate.

In the separation of heavy metals, bivalent Cu can be masked by addition of thiosulfate. The univalent Cu thus formed gives a colorless, stable complex compound of the composition $Na_3[Cu(S_2O_3)_2]$ [8].

During the separation of Al from solution by means of hydroxyquinoline in the presence of PO_4^{3-}, tartaric acid and NH_3 are first added in order to combine with Al to form a complex anion $[Al(Tar)_3]^{3-}$ [9] which is stable in alkaline media.

For elements which are similar to each other in chemical properties, the differences in the stability of complexes of the same kind may be used for separating them to a greater extent than is done at present. Sometimes it is possible to vary the stability of the complex compounds within wide limits. By increasing the acidity e.g. by addition of HNO_3 or H_2SO_4, as a rule, the coordination links of the central atom with the residues can be weakened particularly if the latter are anions of weak acids. HCl and acetic acid are not so suitable for acidification, because their anions form complexes with the metal ions.

On the other hand alkalization sometimes strongly consolidates the complex. Very indicative in this connection are the complex citrates of the rare earth elements of composition $Na_3[Me^{III}(Cit)_2]$ which in acid solutions dissociate practically completely according to the equation

$$Na_3[Me^{III}(Cit)_2] \rightleftharpoons 3Na^+ + Me^{3+} + 2Cit^{3-}.$$

By the addition of NH_3 initially to the neutral solution the citrate complexes are strengthened to such an extent, that the ions of the rare earth elements cannot be precipitated by oxalate or fluoride ions [10].

On acidification of the complex anion $[Fe(CN)_6]^{4-}$, its inner sphere dissociation increases. The simple ions Fe^{2+} thus formed then react with ferrocyanide ions to give blue colored compounds.

Dimethylglyoxime is an equally good reagent for both bivalent Pt and Pd ions. These elements yield complex compounds with $NaNO_2$ which differ appreciably in stability. The instability coefficients of $Na_2[Pt(NO_2)_4]$ is very small and enables Pd to be precipitated by addition of an alcoholic solution of dimethylglyoxime, from a mixture of Pd and Pt after a preliminary nitrite treatment.

In the colorimetric determination of Co with nitroso-R-salt, the elimination of interference from a number of heavy metals (Fe, Ni, Cu, Cr, etc.) is of vital importance, since some of them give colored complexes similar to Co (viz Fe, Cu, Ni)

while Cu and Ni ions are colored themselves. However, because of the difference in stability of the complex compounds formed, on acidification with HNO_3 only the colored compound of Co with nitroso-R-salt persists [11].

In the determination of small amounts of Co present in large amounts of Fe, Ni and Cu, the latter are removed by boiling with excess sodium acetate. Co remains in solution in the form of a stable acetate complex $Na_3[Co(CH_3COO)_6]$. The acetate complexes of Fe, Ni and Cu decompose with separation of $Fe(OH)_3$, $Ni(OH)_2$, and CuO respectively [12].

A method of separating Co in the form of the difficultly soluble compound $Ag_3[Co(CN)_6]$ is based on the different stabilities of the cyanide complex compounds $K_3[Co(CN)_6]$ and $K_4[Ni(CN)_6]$ in acid solution, Ni remains in solution in the form of the simple cation [13].

For the same reason during electrolysis of solutions of the cyanide complexes of Co and Ni, only the latter yields a black precipitate of NiO on the anode.

Os and Ru with excess thiourea form red and blue colored complexes respectively [25]. In order to detect Os in the presence of Ru therefore an excess of diethyldithiophosphoric acid is added to the thiourea complex of these elements; the less stable Ru complex is decomposed. If Os is present, then the solution will be colored the rose or red color of the thiourea complex of Os [45].

Mo always turns up in the colorimetric determination of Re. Both these elements give colored complexes with thiocyanates of the probable composition $K[MoO(CNS)_4]$ and $K[ReO(CNS)_4]$. On strong acidification, only the Re complex remains because of its greater stability [15]. In this case the choice of acid is very important, HCl will not only change the acidity of the medium, but excess of Cl ions is sufficiently strong to act as coordination substitutes and can lead to a change in the composition of the thiocyanate complex of Mo.

In this connection it should be observed that the analyst often has to deal with complex solutions in which different anions exist together with metallic cations. Under such conditions complex formation in the solution must be considered. Different acid radicals and neutral molecules show different tendencies to complex formation with metal ions. The following empirical series was found for bivalent Pt [16, 17]:

$$CN^- > S_2O_3^{2-} > I^- > SCN_2H_4 > SCN^- > NO_2^- > Br^- > C_5H_5N > Cl^- > OH^- > SO_4^{2-},$$
$$NO_3^-, ClO_4^-.$$

In this series tendency to complex formation decreases from left to right. Bivalent Pt forms complexes with the most reactive of these coordination substituents in solution. Similar series could be established for the ions of other metals.

Many difficultly soluble complex compounds give crystals of very characteristic form, which are suitable for identification of the elements. In Korenman's book [18] a fairly large number of such examples are given.

The complex chromooxalate of K, $K_3[Cr(C_2O_4)_3]$ forms characteristic precipitates in the form of green rhomboids under the microscope, only with the first four elements of the rare earth group, the composition is $Me^{III}[Cr(C_2O_4)_3]$, where Me^{III} is La, Ce, Pr, Nd [19]. The majority of other elements do not interfere.

For detecting SO_4^{2-} successfully the thiourea complex of Pt can be used

$[Pt(Thio)_4]Cl_2$. In the presence of SO_4, a very characteristic crystalline precipitate of composition $[Pt(Thio)_4]SO_4$ separates out instantly. Other anions containing S, SO_3^{2-}, $S_2O_3^{2-}$ do not interfere, because they form precipitates different in form and composition, such as $[Pt(Thio)_3SO_3]$ and $[Pt(Thio)_3S_2O_3]_3$ [20].

The formation of difficultly soluble complex compounds could be of far greater significance in gravimetric analysis. In the majority of cases the crystalline precipitates formed do not trap impurities, which is a very characteristic property of bulky precipitates.

The classical method of determining K by means of sodium chloroplatinite is based on the fact that the solubility of the complexes of composition $Me_2^I[PtCl_6]$ where Me = Na, K, Rb, Cs decreases rapidly with the increasing atomic weight of the cation. Such regularities are found in other cases. Thus silicomolybdic acid $H_8[SiMo_2O_7]_6$ gives crystalline, difficultly soluble precipitates with salts of Rb and particularly Cs.

The solubility of complexes of the type $Me_2^I[SnCl_6]$ essentially changes from Li to Cs.

In the reaction of $(NH_4)_2[Hg(CNS)_4]$ with Cu^{2+}, Ag^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, precipitates are formed which differ in solubility, are similar in the constitution of the outer sphere and of the type $Cu[Hg(CNS)_4]$ or the mixed type $(NH_4)_2Co[Hg(CNS)_4]_2$.

Substitution in the outer sphere of K in the cyanide complexes of Fe, $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$, for heavy metal ions leads to formation of difficultly soluble compounds [21].

Of interest is the systematic study of the formation of difficultly soluble compounds; thiocyanates, cyanides, sulfites, oxalates and other complexes.

It is possible to prepare difficultly soluble complexes by substitution in the outer sphere of the complex cations $[Co(NH_3)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$, $[Cu\ en_2]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Cd(NH_3)_4]^{2+}$ and others with the chlorate radical to give e.g. $[Cd(NH_3)_4](ClO_4)_2$ [22].

Anions of organic sulfonic acid also form difficultly soluble compounds, in which the solubility decreases with complexity of the hydrocarbon skeleton of the sulfonic acid $[Cr(NH_3)_6]$ $(C_7H_6NSO_3)_3$; $[Cr(NH_3)_6]$ $(C_{12}H_8N_2SO_3)_3$; $[Cr(NH_3)_6](C_{14}H_7O_4SO_3)_3$.

Practically insoluble complexes can be prepared by combining complex cations and anions, e.g. Magnus' green salt $[Pt(NH_3)_4]$ $[PtCl_4]$.

By the interaction of antipyrine or pyramidone with ions of many of the heavy metals, complex cations are formed of the general composition $[Me(C_{11}H_{12}ON_2)_6]^{2+}$ with high molecular weights.

Complex ammoniate groups can be used as complex cations in precipitation reactions e.g. $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_6]^{2+}$ and other nitrogen derivatives such as $[CdPy_4]^{2+}$, $[ZnPy_4]^{2+}$, $[HgPy_4]^{2+}$ and $[NiPy_6]^{2+}$.

In a number of cases the formation of multi-complexes finds an application in analytical chemistry.

By the action of $[Co(NH_3)_6](NO_3)_2$ on a mixture of the complex fluorides of Be, Mg, Al, Zn and Sc, a precipitate containing only the complex fluoride of Sc can be formed $[Co(NH_3)_6][ScF_6]$ [23].

The slightly stable complex of univalent Cu, $H[CuCl_2]$ forms a difficultly soluble precipitate of the composition $[Pt(NH_3)_4][CuCl_2]_2$ [24].

The formation of multi-complexes of the type $[Me^{III}(C_{11}H_{12}ON_2)_6][Cr(CNS)_6]$ with a very high molecular weight by the action of phenyldimethylpyrazolone on the rare earth elements and a number of other metals is worthy of the analyst's attention [26].

Practically insoluble complex compounds can be obtained in many cases by substitution in the outer spheres of organic cations of the ammonia type, e.g. pyridine (PyH^+), quinoline (XyH^+), antipyrine ($AntH^+$), etc. Such complexes are $(C_5H_5NH)[AuBr_4]$, $(C_9H_7ONH)K_3[Fe(CN)_6]$, $(C_5H_5NH)_2[HgI_4]$, $(C_9H_7ONH)[BiI_4]$ and $(C_{11}H_{12}ON_2H)[HgI_4]$, etc. Gusev used many compounds of a similar type for analytical purposes [27].

Complex compounds of the non-electrolyte type are of special interest in analytical chemistry. Such compounds are easily formed by metals of the Pt group, particularly Pt and Pd, e.g. platinum diammine dichloride $[Pt(NH_3)_2Cl_2]$. $[Pt(Thio)_2Cl_2]$ [28], $[Pt(NH_3)_3S_2C_3]$, $[Pt(Thio)_3S_2O_3]$ and $[Pt(NH_3)_3SO_3]$ are also only very slightly soluble [29].

Similar types of practically insoluble crystalline compounds can be obtained for other metals, e.g. $[Hg(Py)_2Cl_2]$, $[Cd(Py)_2Cl_2]$, $[Pb(Thio)_2Cl_2]$, $[Cu(Py)_2(CNS)_2]$ and $[Ni(Py)_2(CNS)_2]$.

Pt can be separated from Bi by precipitating the Pb with excess thiourea to give a crystalline compound which is practically insoluble and has the probable composition $[Pb(Thio)_2(NO_3)_2]$. Bi remains in solution in the form of a complex compound of the composition $[Bi(Thio)_4](NO_3)_3$ [30].

From a solution containing Cu and Ni, pyridine precipitates Ni in the form $[Ni(Py)_3Cl_3]$ while Cu remains in solution as $[Cu(Py)_4]Cl_2$.

The complex compound of Hg, $K_2[HgI_4]$ reacts differently with pyridine and the pyridine ion, forming difficultly soluble complexes. In the first case the compound formed is $[Hg(Py)_2I_2]$ and in the second $(PyH)_2[HgI_4]$. The compound $[Hg(Py)_2I_2]$ on heating, dissolves and is transformed into $[Hg(Py)_4]I_2$, but on cooling it separates out in the unchanged form again.

Complex compounds are of exceptional importance in chromatographic analysis.

The synthetic resins (SBS, Espatite-1, KU-2, Amberlite, Dowex, Wofatit, etc.) are products of the polymerization of styrene, and the condensation products of phenol and formaldehyde and their derivatives. As a result of special treatment active groups are introduced into their molecules, e.g. $R\text{-}SO_3$, R-COOH, R-OH in the nucleus or side chain. Since the active groups are connected with the skeleton of the resin, they cannot transfer into solution. Only the H ion or cations which have replaced it retain their mobility ($R\text{-}SO_3H$). In this sense the solid phase of the resin represents a strongly dissociated acid or its salt.

The general reaction of ion exchange can be expressed by the equation:

$$\underline{n}\ R\text{-}SO_3H + Me^{n+} \rightleftarrows (R\text{-}SO_3)_nMe + \underline{n}H^+$$

where Me = Na, K, Ca, Mg, Al, Fe.

Ion exchange reactions can be considered as heterogeneous processes between active groups of the resin in a gel phase and the external phase of the solution, which proceed according to the law of mass action.

In the analysis of natural materials and different alloys, the problem can be reduced to a choice of a suitable complex compound former which can form a

complex anion with one of the elements to be determined. The separation of Fe and Al or Fe and Mg is based on the fact that Fe ions being good complex formers with many acid radicals can form complex anions. Even in HCl solutions, Fe exists as $[FeCl_6]^{3-}$ while Al and Mg remain as the simple hydrated cations Al^{3+} and Mg^{2+}. When a solution containing these three elements is passed through a column packed with a cation exchange resin (cationite) in the hydrogen form, Al and Mg are retained on the active groups of the resin; while the complex Fe ion passes through the column unchanged.

$$3R\text{-}SO_3H + Al^{3+} \longrightarrow (R\text{-}SO_3)_3Al + 3H^+.$$

The chromatographic separation of Fe and Cu is a more complicated case. Both these metals are good complex formers. Therefore, in HCl solution both metals are present in the form of complex ions $[FeCl_6]^{3-}$ and $[CuCl_4]^{2-}$, nevertheless separation can still be effected. In the analysis of a bronze ligature, sodium pyrophosphate was chosen [31]; this reacts with Fe and Cu to form complex anions of the composition $[Fe_2(P_2O_7)_3]^{6-}$ and $[CuP_2O_7]^{2-}$. The Cu complex is considerably less stable and on treatment with NH_3 solution it is converted into the complex cation $[Cu(NH_3)_4]^{2+}$. When the mixture thus treated is passed through a column containing a cationite the Fe complex is completely separated from Cu and passes through the column in the form of the complex anion, while the Cu complex cation is retained by the active group of the resin.

$$2R\text{-}SO_3H + [Cu(NH_3)_4]^{2+} \longrightarrow (R\text{-}SO_3)_2[Cu(NH_3)_4] + 2H^+.$$

A mixture of Fe, Al and Cu can be successfully separated by the use of the unequal stability of their citrate complexes. On addition of NH_3 only Fe and Al are transformed into the complex anions $[Fe(Cit)_2]^{3-}$ and $[Al(Cit)_2]^{3-}$, Cu in this case forms the complex cation $[Cu(NH_3)_4]^{2+}$. When the solution is passed through a cationite column, the Fe and Al pass through into the filtrate. The filtrate is then acidified to a pH 1.5 to 2, when the less stable Al anion decomposes and Al is precipitated as the single cation Al^{3+}. A second passage of the solution through the cationite column leads to separation of Fe from Al.

The analysis of ore slime Pt is considerably simplified since on separation from the original solution of the excess HCl, the noble metals appear as complex anions, $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$, etc., while the other, non-noble metals, will be in the form of simple cations Fe^{3+}, Cu^{2+}, Ni^{2+} [32]. After prolonged heating of the HCl solution of the Pt group metals, Ru in the form of a simple cation is completely retained by a cationite while the other elements of this group go into the filtrate in the form of complex ions.

The chromatographic separation of such closely related pairs of elements as Co and Ni can be effected by oxidation to the trivalent state whereby Co is converted into a stable anion while Ni for a sufficient acidity of the solution remains as the simple cation.

By the use of a cationite in combination with radioactive indicators, it is possible to separate elements which resemble each other very closely in chemical properties, such as the alkaline earths or rare earth elements [33]. In the latter case the metals which are retained on the upper part of the column are washed with a solution of complex formers at a definite pH. The problem of separation in this case reduces to finding the range of acidity of the solution produced by organic acids (citric, tartaric, oxalic, etc.) at which a difference can be detected in the instability constants of the complexes of the pairs of elements to be determined [35]. In its progress along the column during washing, the element with the most stable complex anion moves fastest into the filtrate.

Hitherto mention has been made of only a few separations in analytical mixtures effected by means of cation exchange. In some cases anion exchange resins (anionites) can be used for this purpose, but owing to their lower stability to acid and alkalis, this form of synthetic resin is not quite so suitable for analytical purposes as the cationites.

It is of great importance in analytical chemistry that the component parts of the complex (the nucleus and the coordination groups) suffer essential changes as a result of complex formation. It is useful to consider a few examples.

The dioxime forming part of Pd dioxime is easily oxidized to products of complete combustion, while dioxime on its own is oxidized only to intermediate compounds [36].

Oxalic acid titrates with $KBrO_3$ in HCl solution only very slowly and incompletely. The oxalate groups and bioxalate in Pt complexes are just as easily oxidized as with $KMnO_4$ [37].

Aminosulfonic acid even at high temperatures cannot be oxidized by $KMnO_4$ but as a component of the complex $[Pt(NH_3)_2(NH_2SO_3)Cl]$, it is oxidized just as easily as free oxalic acid [38].

Many metallic ions which are components of complex ions are oxidized appreciably more vigorously than when in the form of a simple ion, e.g. $[Ce^{III}(Cit)_2]^{3} \longrightarrow [Ce^{IV}(Cit)_2X_2]^{4-}$, $[Co^{II}(NO_2)_6]^{4-} \longrightarrow [Co^{III}(NO_2)_6]^{3-}$, $[Cu^{I}(NH_3)_2]^{+} \longrightarrow [Cu^{II}(NH_3)_4]^{2+}$.

Weak boric acid in the presence of certain organic compounds can be titrated with phenophthalein as a unibasic acid [39].

Thiosulfuric acid does not exist in the free state, and thiosulfates slowly decompose in acid media. Coordinately bound thiosulfate radicals are stable towards acid, and the complex acid of composition $H_2[Pt(S_2O_3)_4]$ is as strong as H_2SO_4 [40].

During the formation of complex compounds the oxidation-reduction properties of the system change considerably, an important consideration for analytical purposes.

The value of the potential of a complex oxidation-reduction system is determined by the relations of the concentration of ions of oxidizer and reducer not bound up in the complex form. The concentration of single ions in its turn is determined by the instability constants of the complex compound formed, and depends on the concentration of complex forming compounds.

Thus for the systems Fe^{3+}-Fe^{2+} a decrease in the oxidation-reduction potential in H_2SO_4 is observed for the most reactive complex forming compound in the following order H_3PO_4 (0.516 V); $H_2C_2O_4$ (0.462 V); HF (0.422 V); $H_4P_2O_7$ (0.416 V).

For the system VO^{2+}-V^{3+} in H_2SO_4 when phosphoric acid, ammonium fluoride are used as complex formers, it is possible to get solutions with potential values in the range 0.621 to 0.279 V [41].

The constituents of complex compounds are susceptible in a series of cases to successive oxidation. Thus in the compounds $[Pt(NH_3)_4]$, $[Pt(CN)_4]$, Pt in the complex cation and anion is oxidized separately, and is expressed on the potentiometric titration curve by two steps for different potential values [42]. In the Pt-bioxalate of composition $[Pt(NH_3)_2(HC_2O_4)_2]$ the bioxalate group and the Pt are titrable in a definite order; first the Pt and then the bioxalate

groups successively [43]. In the thiosulfatoplatinite complex $K_2[Pt(NH_3)_2(S_2O_3)_2]$ on oxidation with bromate the following order is observed. $S^{2-} \rightarrow S^0$ (1 step), $Pt^{2+} \rightarrow Pt^{4+}$ (2 steps) and $S^0 \rightarrow S^{6+}$ (3 steps) [44].

The examples quoted here by no means exhaust all the multitude of possibilities of applying complex compounds in analytical chemistry.

In conclusion we would like to express the hope that there will be a considerable expansion in the number of investigations in the application of complex compounds in analytical chemistry.

LITERATURE CITED

[1] Ilinsky, Ber. 17, 2592 (1884); 18, 699 (1885).

[2] L. A. Chugaev, Ber. 39, 3382 (1906).

[3] S. A. Voznesensky, Inner complex compounds and their significance for analytical chemistry. State Institute of Technology, 1938.

[4] V. I. Kuznetsov, J. Gen. Chem. 20, No. 5, 807 (1950)[1]; J. Anal. Chem. 6, No. 3, 139 (1951).

[5] D. I. Ryabchikov, J. Appl. Chem. 17, No. 4-5, 284 (1944), 1949.

[6] A. K. Babko, J. Gen. Chem. 16, No. 10 (1946).

[7] D. P. Malyuga, Proc. Acad. Sci. 48, No. 2, 119 (1945).

[8] D. I. Ryabchikov, V. G. Silnichenko, Bull. Acad. Sci. Div. Chem. Sci. No. 1, 19 (1947).

[9] R. Berg, The use of o-hydroxyquinoline in analytical chemistry, United Sci-Tech Press, (1937), p. 62.

[10] D. I. Ryabchikov, E. A. Terenteva, Proc. Acad. Sci. 58, No. 7, 1373 (1947).

[11] D. P. Malyuga, Methods of Determining Micro Elements, USSR Acad. Sci. Press, 1950, p. 45.

[12] D. P. Malyuga, J. Anal. Chem. 2, No. 6, 323 (1947).

[13] F. Rodgers, Phil. Mag. 4, 98 (1834).

[14] V. S. Saltykova, Proc. Acad. Sci. 49, No. 1, 34 (1945).

[15] Kh. G. Vinogradova, Methods of Determining Micro Elements. USSR. Acad. Sci. Press, 1950, p. 69.

[16] D. I. Ryabchikov, Bull. Sect. Platinum Inorg. Gen. Scient. Chem. Acad. Sci. No. 20, 42 (1946).

[17] A. A. Greenberg, Introduction to the chemistry of complex compounds, 2nd Edit; State Chem. Press, 1951.

[18] I. M. Korenman, Microcrystalloscopy, State Chem. Press, 1947.

[19] D. I. Ryabchikov and E. A. Terenteva, Bull. Acad. Sci. Div. Chem. Sci. No. 1, 44 (1949).

[20] D. I. Ryabchikov, Proc. Acad. Sci. 18, No. 1 (1938).

[21] I. V. Tananaev, and M. I. Levina, J. Anal. Chem., 1, 224 (1946), 3, 31 (1948); Fact. Lab. 15, 887 (1949).

[22] I. V. Tananaev and S. Ya. Levitman, J. Anal. Chem., 5, No. 4, 212 (1949).

[1]) See Consultants Bureau English translation, p. 845.

[23] V. V. Shcherbina, Prog. Chem. No. 11-12 (1939).

[24] D. I. Ryabchikov, S. V. Nersesova, Bull. Sect. Platinum 18, 100 (1945).

[25] L. A. Chugaev, Comptes rend. 167, 235 (1918).

[26] D. I. Ryabchikov and E. A. Terenteva, Proc.. Acad. Sci. 51, No. 4, 287 (1946).

[27] S. I. Gusev, J. Anal. Chem. 5, No. 6, 375 (1950).

[28] N. S. Kurnakov, Selection of Collected Works, Vol. 1, 1938, p. 69.

[29] D. I. Ryabchikov, N. B. Lyubimova, Bull. Sect. Platinum 25, 176 (1950).

[30] C. Mahr, H. Ohle, Z. anorg. Chem. 234, 224 (1937).

[31] L. Wohler, L. Metz, Z. anorg. Chem. 138, 368 (1924).

[32] D. I. Ryabchikov, E. A. Terenteva, Prog. Chem. 19, No. 2, 220 (1950).

[33] A chromatographic method of separating ions. Coll. of Articles under editorship of E. N. Gapon, 1949.

[34] Street, Seaberg, J. Am. Chem. Soc. 70, 4268 (1948).

[35] D. I. Ryabchikov. . A Chromatographic Method of Separating Ions. Coll. edited by E.N.Gapon, 1949.

[36] V. S. Syrokomsky, S. M. Gubelbank, J. Anal. Chem. 4, No. 4, 203 (1949).

[37] D. I. Ryabchikov, A. A. Greenberg, J. Phys. Chem. 12, No. 1, 59 (1938).

[38] D. I. Ryabchikov, Bull. Sect. Platinum, 20, 139 (1947).

[39] S. I. Sinyakova, Methods of determining microelements, USSR Acad. Sci. Press, 1950.

[40] D. I. Ryabchikov, Bull. Sect. Platinum 21, 105 (1948).

[41] V. S. Syrokomsky, V. B. Avilov, Factory Lab. 16, No. 1 (1949).

[42] A. A. Greenberg, D. I. Ryabchikov, Proc. Acad. Sci. 14, No. 3, 117 (1937).

[43] A. A. Greenberg, D. I. Ryabchikov, Acta Phys. Chim. USSR, 8, 773 (1938).

[44] D. I. Ryabchikov, Proc. Acad. Sci. 33, No. 3, 233 (1941).

[45] A. I. Busev, J. Anal. Chem. 4, No. 1, 49 (1949).

THIOUREA COMPLEXES OF LOW SOLUBILITY AND THEIR APPLICATION IN ANALYSIS

K. B. Yatsimirsky and A. A. Astasheva

(Ivanovsky Institute of Chemical Technology)

Complex compounds with thiourea have attracted the attention of many investigators for a long time. After the first synthesis of thiourea complexes [1, 2, 3] which were of a rather haphazard nature, the classical investigations of Kurnakov [4,5] appeared. N. S. Kurnakov, who synthesized new complex compounds with thiourea, proved their structure and compared the thiourea complexes with other complex compounds and finally turned his attention to the fact that stable complexes are formed with metals which are precipitated in acid media by H_2S.

Thiourea complexes were further studied by Chugaev [7,8], Lebedinsky [9,10], Rosenheim and Meyer [6], Mahr and Ohle [11] and others. In the course of these investigations the order of the changes in stability of thiourea complexes was established [6] and a number of practically insoluble salts, consisting of complex cations and large anions were isolated [8,9,10,11].

Chugaev [7] was the first to use thiourea for analytical purposes (for isolating Os); further Mahr and Ohle [11] worked out a number of analytical methods based on the use of thiourea complexes.

Thiourea gives complex compounds with cations which possess a clearly defined tendency to form covalent bonds, and are characterized by large values of the difference between ionization potential and the heat of hydration [13]. Large complex cations of the type $Me(CSN_2H_2)_n]^{z+}$ formed according to equation (1) should be precipitated by large anions [12,13] (e.g. tetrathiocyanodiamminochromite, tetranitrodiamminocobaltite, picrate, etc.).

$$Me^{z+} + nCSN_2H_4 = [Me(CSN_2H_4)_n]^{z+} \qquad (1)$$

$$[Me(CSN_2H_4)_n]^{z+} + zX^- = [Me(CSN_2H_4)_n]X_z. \qquad (2)$$

In order to prove this, to 0.03 molar solutions containing the cations Ag^+, Tl^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Bi^{3+}, Sb^{3+} [1], Fe^{3+}, Cr^{3+} and Al^{3+}, respectively was added a molar solution of thiourea, and afterwards to separate lots, saturated solutions of potassium picrate, ammonium tetrathiocyanodiamminochromite (Reinecke's salt) and ammonium tetranitrodiamminocobaltite (Erdman's salt) were added respectively. (The volume of solution taken amounted to approximately 0.3–0.4 ml). In the case of solutions of Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Sb^{3+}, Fe^{3+}, Cr^{3+}, and Al^{3+}, no precipitates were formed. While Ag^+, Tl^+, Cu^+, Hg^{2+}, Cd^{2+}, Pb^{2+}, and Bi^{3+}, which formed fairly stable complex cations with thiourea in solution, were precipitated by the large anions.

The crystal form of the precipitates was studied as well as the sensitivity of the reactions in drops of volume 0.003–0.004 ml. All the reactions were carried out in neutral or weakly acid solution, since precipitates of the sulfides of the respective metals are usually precipitated in alkaline media.

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1) A solution of $SbCl_3$ in HCl was used.

The new compounds isolated were chemically analyzed and are described below.

1. COMPLEX BISMUTH SALTS

On addition of thiourea to a solution of bismuth nitrate, an intense yellow complex compound is formed. When a solution of Reinecke's salt is added to this crystals of characteristic form are precipitated (Fig. 1).[1)]

The salt corresponds to the formula $[Bi(CSN_2H_4)_6][Cr(NH_3)_2(CNS)_4]_3$. Concentration limit 1:18000; Limit of identification 0.17 µ g.

Calculated (%)	Found (%)
Cr 9.63;	9.44; 9.50; 9.71.
CSN_2H_4 28.20;	28.27; 28.33; 28.42.

The action of Erdman's salt on the solution of the bismuth complex does not yield a precipitate. The picrate ion and Reinecke's salt both precipitate basic salts of Bi in the absence of thiourea (from concentrated solution).

2. COMPLEX MERCURY SALTS

From solutions of Hg salts Reinecke's salt separates intensely colored precipitates, which are practically insoluble in water and do not change appreciably on addition of thiourea. On addition of a solution of K picrate to a solution of $Hg(NO_3)_2$ and thiourea, characteristic crystals of the difficultly soluble salt of composition $[Hg(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ (Fig. 2)[1)] separate out.

Concentration limit 1;35000; limit of identification 0.086 µg.

Calculated (%)	Found (%)
Hg 20.88;	20.86.
CSN_2H_4 31.64;	31.31.

3. COMPLEX CADMIUM SALTS

Solutions of Cd salts react with thicurea to form a fairly stable complex ion, which can be precipitated by picrate and Reinecke's salt. The addition of Erdman's salt to solutions of Cd not containing halides, does not lead to the formation of a precipitate.

The sensitivity of the reaction of formation of the tetrathiocarbammide-picrate is characterized as follows:

Concentration limit 1:91000; limit of identification 0.033 µg.

Calculated (%)	Found (%)
Cd 12.88;	12.79; 12.82.
CSN_2H_4 34.84;	34.83; 34.52; 34.55.

The composition corresponds to $[Cd(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ (Fig. 3)[1)].

The formation reaction of the corresponding complex with Reinecke's salt is fairly sensitive. Concentration limit 1;135000; limit of identification 0.022 µg. The crystal form is depicted in Fig. 4.[1)]

The compound $[Cd(CSN_2H_4)_2]$ $[Cr(NH_3)_2(CNS)_4]_2$ was described by Mohr and Ohle [11]. On analysis we got different results, the composition being better represented by the formula $[Cd(CSN_2H_4)_4]$ $[Cr(NH_3)_2(CNS)_4]_2$, although in some preparations the content of the thiourea is lower. It is possible that in such a case a mixture of complexes is formed with different numbers of coordinated thiourea groups.

[1)] See Plate, page 79.

4. COMPLEX LEAD SALTS

Picrate precipitates a comparatively difficultly soluble salt of the composition $[Pb(CSN_2H_4)_4](C_6H_2N_3O_7)_2$ from solutions containing complex ions of Pb with thiourea. The pale yellow crystals formed have the form shown in Fig. 5.[1)]

Concentration limit 1:3200; limit of identification 1.43 µg. Analysis of the salt obtained gave the following results:

Calculated (%)	Found (%)
Pb 21.42;	21.03.
CSN_2H_4 31.43;	31.31.

Reinecke's salt precipitates Pb in the form of an amorphous precipitate which does not change significantly on the addition of thiourea. Addition of Erdman's salt to a solution of Pb and thiourea does not yield a precipitate.

5. COMPLEX THALLIUM SALTS

If thiourea and then picrate are added in that order to a solution containing Tl a crystalline precipitate is formed (Fig. 6).[1)]

The sensitivity of the reaction is given by the following result: Concentration limit 1:87000; limit of identification 0.035 µg.

The precipitate obtained was not analyzed.

Reinecke's salt precipitates an amorphous precipitate from solution of Tl; Erdman's salt does not form a precipitate with a solution of Tl salts or with the thiourea complex compound.

6. SILVER COMPLEX SALTS

Ag ions form very stable complex ions with thiourea of the composition $[Ag(CSN_2H_4)_2]^+$. On addition of picrate to a solution of an Ag salt containing excess thiourea, a characteristic crystalline precipitate is formed (Fig. 7).[1)]

This reaction is one of the most sensitive of known analytical reactions; in this case the concentration limit is 1:1500000 and the limit of identification 0.0027 µg. Halides do not interfere. The composition of the precipitate corresponds to the formula: $[Ag(CSN_2H_4)_2](C_6H_3N_3O_7)$ as the analytical results show.

Calculated (%)	Found (%)
Ag 22.10;	22.09; 21.98.
CSN_2H_4 31.14;	30.85.

The complex ions $[Ag(CSN_2H_4)_2]^+$ are precipitated also by Erdman's salt, forming characteristic crystals (Fig. 8).[1)]

The sensitivity of this reaction is considerably lower than the reaction with the picrate.

Concentration limit 1:9300; limit of identification 0.43 µg. The precipitate obtained dissolves in an excess of thiourea and behaves similarly to other thiorea complexes of Ag,e.g. $[Ag(CSN_2H_4)_2]Cl$. Apparently in such a case complex ions are formed in solution with a higher coordination number.

The reaction considered is specific for Ag, only Cu interferes. Result of the analysis was $[Ag(CSN_2H_4)_2][Co(NH_3)_2(NO_2)_4]$.

[1)] See Plate, page 79.

Calculated (%)	Found (%)
Ag 20.20;	19.86.
CSN_2H_4 28.47;	28.06.

Reinecke's salt precipitates an amorphous precipitate of $Ag[Cr(NH_3)_2(CNS)_4]$ which does not change appreciably on addition of thiourea.

7. COMPLEX COPPER SALTS

Salts of bivalent Cu are reduced by thiourea to thiourea complexes of univalent Cu. Picrates separate from solutions of these complexes, characteristic crystals (Fig. 9).[1]

Concentration limit 1:43000; limit of identification 0.069 μg. The formula of this salt $[Cu(CSN_2H_4)_3](C_6H_2N_3O_7)$ was confirmed by analysis.

Calculated (%)	Found (%)
Cu 12.23;	12.12; 12.19; 12.23.
CSN_2H_4 43.88;	43.53; 43.79.

Erdman's salt does not precipitate thiourea complexes of Cu salts (I) but the Cu salts form an amorphous precipitate with Reinecke's salt.

A few results are compared in the following table.

Table

The precipitation of the thiourea complexes of metals by large anions

Thiourea complexes with ions	Limits of identification for anion action		
	picrate μg	tetrathiocyanoammino chromite, Reinecke's salt, in μg	tetranitrodiammino cobaltite, Erdman's salt, in μg
Bi^{3+}	not studied	0.17	no ppt.
Hg^{2+}	0.086	amorphous ppt.	"
Cd^{2+}	0.033	0.22	"
Pb^{2+}	1.43	amorphous ppt.	"
Zn^{2+}	no ppt.	"	"
Ag^{+}	0.0027	"	0.43
Tl^{+}	0.035	"	no ppt.
Cu^{+}	0.069	"	"

Consequently the formation of thiourea complex cations and their precipitation by large anions can be used for the detection of cations which have a tendency to form stable donor-acceptor bonds. Of the triple charge ions it is possible to detect only Bi^{3+} in this way; this is characterized by the largest value of the covalent characteristic (K = 290). Only complexes with covalent characteristics greater than 150 kcal are precipitated from solutions of double charged ions, containing excess thiourea, by large anions. The ion of Zn^{2+} with K = 136 kcal; although it forms complex compounds with thiourea in aqueous solution, these complexes are not precipitated by large anions, apparently as the result of a lack of stability in the complexes.

All unicharged ions having 18 or 18 + 2 electrons in the outer orbit have high values for the covalent characteristic and can be found in the form of thiourea complexes by means of large anions.

SUMMARY

1. New, practically insoluble complex compounds of thiourea with large anions in the outer spheres have been prepared:

$[Bi(CSN_2H_4)_2][Cr(NH_3)_2(CNS)_4]_3$; $[Hg(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; $[Cd(CSN_2H_4)_2](C_6H_2N_3O_7)_2$; $[Pb(CSN_2H_4)_4](C_6H_2N_3O_7)_2$; $[Ag(CSN_2H_4)_4](C_6H_2N_3O_7)$; $[Ag(CSN_2H_4)_2][Co(NH_3)_2(NO_2)_4]$; $[Cu(CSN_2H_4)_3](C_6H_2N_3O_7)$.

2. The compounds prepared have characteristic crystalline forms. The formation of such compounds can be used for the detection of Bi^{3+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}, Tl^{+} microcrystalloscopically. The sensitivity of these reactions was determined.

3. The formation of thiourea complexes in solution and their precipitation by large anions is a reaction typical for cations with a large covalency characteristic [13].

Received May 15, 1950.

LITERATURE CITED

[1] J. E. Reynolds, C., 1869, 369.

[2] A. Claus, Ber. 9, 226 (1876).

[3] R. Maly, Ber. 9, 172 (1876).

[4] N. S. Kurnakov, J. Russ. Phys. Chem. Soc. 23, 559 (1891).

[5] N. S. Kurnakov, J. Russ. Phys. Chem. Soc. 25, 565 (1893).

[6] A. Rosenheim, V. Meyer, Z. anorg. Chem. 49, 19 (1906).

[7] L. A. Chugaev, Comptes rend. 167, 235 (1918).

[8] L. A. Chugaev, Bull. Soc. chim. de France (4), 23, 377 (1918).

[9] V. V. Lebedinsky, Bull. Sect. Plat. 12, 79 (1935).

[10] V. V. Lebedinsky, Bull. Sect. Plat. 12, 93 (1935).

[11] C. Mahr, H. Ohle, Z. anal. Chem. 109, I (1937), 115, 254 (1939).

[12] K. B. Yatsimirsky, Bull. Sect. Phys. Chem. Anal. 19, 202 (1949).

[13] K. B. Yatsimirsky, J. Anal. Chem. 6, 211 (1951).

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THE APPLICATION OF MATHEMATICAL METHODS FOR EVALUATING THE RESULTS OF CHEMICAL ANALYSIS[1)]

E. G. Gracheva

The increased demands of our country's industry for high grade analyses compells us to reexamine the mathematical methods used by analysts for evaluating the errors of their results. In a number of cases, e.g. in the calculation of the magnitude of the permissible variation between the results of parallel batches in standard analysis, the approximate evaluation of the errors should be replaced by exact calculations. In order to achieve this it is recommended that the methods of contemporary mathematical statistics be used.

The proposed methods of mathematical treatment can be applied only to errors which are of a random character, i.e. the errors are distributed along a Gaussian curve. The methods are based on the application of new methods from the theory of errors developed by Romanovsky [1]. The advantage of this method as compared with older methods is that it gives more accurate results in the evaluaton of a small number of observations. These methods enable systematic errors (the absence of which ensures the "correctness" of the analytical method employed) to be exposed, by establishing the reality of the deviations between results obtained by different analytical methods, and by discarding results which are distorted by coarse errors.

Since we have not decided on the final choice of terms which reflect the effect of different kinds of errors in results obtained by any method, in any subsequent use of the term "precision"[2)] for the characterization of the method or result, we have in view only errors (mistakes) of a random nature.

I. THE QUANTITATIVE EVALUATION OF THE PRECISION OF A METHOD

The precision of a method is established from n replicate analyses of one and the same material and is characterized by the root mean square value of the error of one single determination, calculated according to the following formula:

$$S = \pm \sqrt{\frac{(a-x_1)^2 + (a-x_2)^2 + \cdots + (a-x_n)^2}{n-1}} \qquad (1)$$

where a is the arithmetic mean, x_1, $x_2 \ldots$, x_n – the analytical results, n is the number of analyses.

For characterization of the precision of a method it is more convenient to express the root mean square value as a percentage, i.e. in the form

$$\frac{S}{a} 100\%. \qquad (1a)$$

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1) A report read at the Conference on Classical Methods of Chemical Analyses held in Moscow, November 14-17, 1951.

2) The choice of this term instead of the more often used "reproducibility" is based on the fact that in metrology and the mathematical theory of errors it is applied to the same category of errors, i.e. to random errors.

In many cases it is necessary to indicate the limits for a change in the magnitude of the error of a single observation, e.g. for evaluation of the permissible variation between results obtained by one method. In such a case the width of the limits will be connected with the probability of finding errors within these limits. (This probability is often called the "confidence" and is designated by α). Thus from the classical theory of probability, it is known that the random error of a single measurement can be greater than the root mean square value S in 32% of all cases (which corresponds to a confidence $\alpha = 0.68\%$), greater than 2S in 5% of all cases ($\alpha = 0.95$) and greater than 3S in only 0.3% ($\alpha = 0.99$).

The possibility of applying the classical methods of calculating errors is excluded for a small number of errors. The methods of contemporary methematical statistics specially developed for a small number of observations must be used instead.

The value of the smallest error of a single observation in this case is expressed in the form $t_\alpha S$, where the factor t_α depends not only on the confidence α but also on the number of experiments (n).

Tables are available [1,2,3] in which the numerical values of t_α for different α from 0.1 to 0.999 and $k = n - 1$ from 1 to infinity are given.

For the same value of α, the magnitude of t_α decreases with increase in k, e.g.

at $\alpha = 0.95$ for	$n = 3$	$t_\alpha = 4.3$	at $\alpha = 0.99$ for	$n = 3$	$t_\alpha = 9.9$
	$n = 5$	$t_\alpha = 2.8$		$n = 10$	$t_\alpha = 3.2$
	$n = 10$	$t_\alpha = 2.3$		$n = 20$	$t_\alpha = 2.9$
	$n = 20$	$t_\alpha = 2.1$			

From this it follows that the width of the interval for all possible values of the error of a single observation (for a definite confidence) can be evaluated more accurately, the greater the number of results used for calculating the root mean square error. This also holds for the accuracy of the determination of S itself, and should be borne in mind in selecting the number of results for characterization of the precision of a method. The table of values for the relative errors (q) for the root mean square error (S) given by Romanovsky [1], shows that for

$\alpha = 0.95$ for	$n = 3$	$q = 340\%$	at $\alpha = 0.99$ for	$n = 3$	$q = 998\%$
	$n = 6$	$q = 109\%$		$n = 6$	$q = 200\%$
	$n = 21$	$q = 36\%$		$n = 21$	$q = 56\%$

Thus the accuracy of S itself obtained from 6 parallel results amounts to only ca. 100% for a confidence of 0.95.

II. EVALUATION OF ANALYTICAL RESULTS AND CALCULATION OF THE RESULTS WHEN GREAT PRECISION IS REQUIRED.

a) The arithmetic mean a obtained from the results $x_1, x_2, \ldots, x_n$ of all the analyses carried out can serve as a result, with an indication of the value of the error calculated for a definite confidence - α. It is necessary to indicate the number of analyses n and the value of the confidence used in order to evaluate the error. (Elimination of results which are obviously spurious from a series of observations can only be carried out by the method given below.)

The answer is given in the following form:

$$A = a \pm t_\alpha \frac{S}{\sqrt{n}} \qquad \text{or} \qquad A = a \pm t_\alpha \frac{S}{a\sqrt{n}}\ 100\% \qquad (2)$$

where $\underline{S}$ is the root mean square error

t_α is the factor depending on the number of analyses $\underline{n}$ and the confidence $\alpha = 0.95 - 0.99$ found from tables.

b) If for the analyses a method is employed the precision of which has been determined beforehand, i.e. the value of S is known, then it is possible to indicate in advance what number of parallel determinations it is necessary to carry out in order to get a result with a permissible error. Let the precision of any method be expressed in percentages by the quantity $\underline{l} = \frac{S}{a}\ 100\%$.

If e.g. it is required to determine the content of any element in a test with an error not greater than p%, then from the formula given above it follows that

$$p = \frac{t_\alpha S}{a\sqrt{n}}\ 100\% \quad \text{whence} \quad n = t_\alpha^2 \left(\frac{l}{p}\right)^2 \qquad (3)$$

Taking the value t_α from the tables [1], we find:

1) $\alpha = 0.95$ for $\frac{p}{l} = 1$ $n = 7$ 2) $\alpha = 0.99$ for $\frac{p}{l} = 1$ $n = 11$

$\frac{p}{l} = 0.5$ $n = 18$ $\frac{p}{l} = 0.5$ $n = 31$

$\frac{p}{l} = 0.1$ $n = 387$ $\frac{p}{l} = 0.1$ $n = 668$

It follows that it is very difficult in practice to get an error with sufficient confidence, which exceeds the precision of the method employed.

III. COMPARISON OF TWO RESULTS AND THE ELIMINATION OF RESULTS WHICH ARE OBVIOUSLY SPURIOUS FROM A SET OF OBSERVATIONS.

a) Comparison of two results $\underline{a}_1$ and $\underline{a}_2$, obtained, e.g. for one and the same test by different analysts in different laboratories or by different methods. We assume that in one series $\underline{n}_1$ analyses were carried out and the average value obtained is $\underline{a}_1$. In another series $\underline{n}_2$ analyses were performed and the mean obtained $\underline{a}_2$.

It is required to explain whether the deviation between the means of the 2 series is the consequence of random errors which are related to the accuracy of the methods, or the results of the two series are essentially different, i.e. in one of the methods at least the error is systematic.

The answer can be obtained from the following formulas.

$$t = \frac{a_1 - a_2}{S_0\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \qquad (4)$$

where

$$S_0 = \sqrt{\frac{(n_1-1)S_1^2 + (n_2-1)S_2^2}{n_1 + n_2 - 2}}$$

S_1 and S_2 are the root mean square errors from the two sets. The numerical value of t for a chosen confidence α is found from the tables for t [1] in this case $k = n_1 + n_2 - 2$.

If after substitution in formula (4) of the values a_1, a_2, S_0 it appears that the value of t_α is greater than or equal to the tabular value of t_α for given values of α and $k = n_1 + n_2 - 2$ it follows that the deviation between comparable values is not random and they must be considered as essentially different.

b) Elimination of results which are obviously spurious can be carried out by the formula given above (4).

Let there be $n + 1$ results:

$$x_1, x_2 \ldots x_n, x_{n+1}.$$

The question posed is whether x_{n+1} is a true result or not, and whether it can be eliminated. The following method is employed. For a series of n results which does not include the doubtful result x_{n+1}, the arithmetic mean $\bar{x}_n$ and the root mean square S are calculated for the n results.

The values found are substituted in formula (4) in which $a_1 = x_{n+1}$ and $n_1 = 1$.

From which it follows that it is difficult in practice to get an error exceeding the precision of the method employed. The same procedure as above is adopted with the result obtained after substitution in the formula. If the deviation between $\bar{x}_n$ and x_{n+1} is not random, then the result x_{n+1} can be eliminated from the series of observations since it is spurious.

We intend to include examples of the application of the methods given above for the evaluation of numerical data obtained by chemical analysts in a future article.

In the literature cited above numerous examples are given, chiefly from technical subjects.

SUMMARY

1. In evaluating the results of a small number of analyses it is necessary to use the new mathematical statistics.

2. The quantitative evaluation of the precision of an analytical method is accomplished by means of the root mean square error, expressed in %, with an indication of the number of analyses from which this value was calculated.

3. The precision of a result (arithmetic mean) obtained by analysis is evaluated for a confidence $\alpha \geqslant 0.95$ according to the root mean square with an indication of the number of replicate experiments.

4. For a small number of results the error calculated by the new statistics is always greater than that calculated from the classical methods.

5. Systematic errors can be detected only by comparison of results obtained by different analytical methods, for conditions where the errors of comparable results or the precision of the methods used are known.

6. A criterion is given for elimination of obviously spurious results.

LITERATURE CITED

[1] V. I. Romanovsky, Basic Problems of the Theory of Errors, 1947.

[2] A. M. Dlin, Mathematical Statistics in Technics, 1951.

[3] N. Arlei and R. Bukh, Introduction to the Theory of Probability and Mathematical Statistics, 1951.

[4] M. F. Malikov, Fundamentals of Metrology, 1949.

MICROCRYSTALLOSCOPIC REACTIONS FOR NITRATES AND NITRITES

N. M. Korenman and A. A. Belyakov

Gorky Institute of Labor Hygiene

A few microcrystalloscopic reactions for nitrates and nitrites are described in the literature. Solutions of nitron and of berberine sulfate in acetic acid form crystalline precipitates with solutions of nitrates and nitrites. These reactions are sensitive (limits of identification from 0.005 to 0.4 μg NO^-_3 NO^-_2) but not specific. In order to increase the specificity of the reaction for nitrite it is carried out in a gas cell. The formation of a crystalline precipitate $K_2PbCu(NO^-_2)_6$ when solutions of nitrites are mixed with acetic acid solutions of the acetates of K, Pb and Cu is also used, but the reaction though specific is of low sensitivity [1].

During the study of the analytical properties of certain mercuri-ammino compounds of the aromatic and heterocyclic series, we worked out several microcrystalloscopic reactions for nitrates and nitrites.

There is no information in the literature on the microcrystalloscopic reactions with mercury organic compounds. We found only a reference to the composition of some crystalline precipitates which are formed during the reaction of metallo-organic compounds with nitrates and nitrites [2]. This enabled us to apply some mercury organic compounds for the microcrystalloscopic reactions for anions.

REACTIONS FOR NITRATES

The reagent which we used was a saturated aqueous solution of 1,4-aminophenylmercuriacetate, which we synthesized according to a method described in the literature [3]; with aqueous nitrate solutions it forms characteristic crystalline precipitates of the composition $H_2NC_6H_4HgNO_3$ in the form of colorless, sharply profiled rosettes of X-shaped crystals, the prisms had sizes up to 170μ. The precipitate settles out from dilute solution on rubbing with a glass rod (Fig. 1). [1])

Limit of identification 0.3 μg NO^-_3.
Concentration limit 1:7000.

The pleocroism of crystals of 1,4-aminophenylmercuriacetate is intense (yellow, red); the extinction angle of the prisms is 7-8°. Ions of Cl^-, Br^-, I^-, CN^-, CNS^-, NO_2^-, S^{2-}, SO_3^{2-}, SO_4^{2-} and some other ions interfere with the reaction. Cl' and SO_4^{2-} also form characteristic crystalline precipitates; Cl' fine transparent rosettes, SO_4^{2-} large rosettes of serrated laminas.

In the presence of nitrites the reaction was performed as follows: to 1-2 drops of the test solution is added a drop of a saturated solution of meta, or better ortho, nitraniline, and the mixture acidified with a drop of 10% acetic acid. On addition of a drop of the solution thus prepared to a drop of the reagent, it is possible to observe the formation of crystals of 1,4-aminophenylmercurinitrate after 5-7 minutes. An amount of NO_2^- equivalent to 20 times that of NO_3 ions (for 0.8 μg NO_3^-) does not interfere.

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[1]) See Plate, page 79.

Nitrates can be detected in solutions containing other ions after these ions have been removed. To 1-2 drops of the test solution a drop of an aqueous solution of Ag acetate (for separation of Cl^-, Br^-, I^-, CN^-, CNS^-) or a drop of a 10% solution of lead acetate (for removal of S^{2-}, SO_3^{2-}, SO_4^{2-}), respectively are added. The solution is then centrifuged and a drop of reagent added to a drop of the transparent centrifugate. The formation of crystals of 1,4-aminophenylmercurinitrate is studied microscopically. It is possible to detect NO_3^- ions (2-3 µg) in the presence of a tenfold excess of interfering ions after their removal by the method just described. Crystals of the reagent and of 1,4-aminophenylmercurinitrate differ appreciably from each other. The crystals of reagent which settle out when a drop dries out consist of colorless parallellograms and rhombic prisms (Fig. 2).[1] The pleochroism of reagent crystals is intense (yellow, red, green); the extinction angle for the crystals is 40°.

Reactions for Nitrites

Eight of the mercury organic compounds which we examined form crystalline precipitates with nitrites viz: 1,4-aminophenylmercuriacetate $H_2N \cdot C_6H_4HgAc$; 1,4-methylaminophenylmercuriacetate $(CH_3)NH \cdot C_6H_4HgAc$; 1,4-ethylaminophenylmercuriacetate $(C_2H_5)NH \cdot C_6H_4HgAc$; 1,4-dimethylaminophenylmercuriacetate $(CH_3)_2N \cdot C_6H_4HgAc$; 1,4-diethylaminophenylmercuriacetate $(C_2H_5)_2N \cdot C_6H_4HgAc$; 2-chloro-1,4-aminophenylmercuriacetate $Cl(NH_2)C_6H_3HgAc$; 2-aminopyridine-5-mercuriacetate $C_5H_3N \cdot (NH_2) \cdot HgAc$; and quinolinemercuriacetate $C_9H_6N \cdot HgAc$.

Some of these compounds either did not form crystalline compounds with solutions of nitrites when a gas cell was used or gave insensitive reactions that makes their application as reagents for nitrites difficult. Detection of nitrites can be carried out in a gas cell with 1,4-aminophenylmercuriacetate; 1,4-methylamino-and 1,4-ethylaminophenylmercuriacetates, and quinolinemercuriacetate. Acetic acid solutions of 1,4-methylamino-and 1,4-ethylaminophenylmercuriacetate form crystalline precipitates of nitrosamines with nitrites [2], aqueous and acetic acid solutions of quinolinemercuriacetate form a precipitate of the corresponding nitrite. 1,4-Aminophenylmercuriacetate does not give a crystalline precipitate with solutions of nitrites when the reaction is carried out in a gas cell, but if the NO_2^- separated out from its acid solution is oxidized to NO_3^- then the presence of NO_2^- can be established by the reaction for nitrates.

In Table 1 results are given which characterize the crystalline precipitates which are formed when these reagents react with nitrite solutions (in a gas cell).

These reactions were carried out as follows; a drop of the test solution was placed at the bottom of the gas cell and acidified with a drop of 10% acetic acid. The cell was covered with a glass plate on the lower surface of which a drop of a mixture of 1,4-aminophenylmercuriacetate and H_2O_2 had been placed (4 vols of a saturated aqueous solution of 1,4-aminophenylmercuriacetate and 1 vol. H_2O_2). The NO_2 liberated from the drop was oxidized by the H_2O_2 to NO_3^-. After 2-3 minutes the drop on the upper glass of the cell was combined with a drop of the reagent (without H_2O_2) and 1,4-aminophenylmercurinitrate was formed, predominantly in the form of prisms, and rods up to 50 µ in size. I^-, CN^-, CNS^- interfere, therefore, they must be removed beforehand as described above. I^- interferes because of the formation of free I_2 according to the reaction:

$$2NO_2^- + 2I^- + 4H^+ = I_2 + 2NO + 2H_2O.$$

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1) See Plate, page 79.

Table 1

Characteristics of Crystalline Precipitates

	Reagent		
	1,4-methylamino-phenylmercuri-acetate	1,4-ethylaminophenyl-mercuriacetate	Quinolinemercuri-acetate
Solvent	8% acetic acid	6% acetic acid	Water
Color, form of crystalline ppt.	Colorless, pale yellow plates, rosettes, needles	Pale yellow plates and rosettes	Colorless six-sided rods, rosettes
Composition of ppt.	$CH_3(NO)N \cdot C_6H_4HgAc$	$C_2H_5(NO)N \cdot C_6H_4HgAc$	$C_9H_8N \cdot HgNO_2$
Limit of identification in μg	0.6	1.6	0.6
Max. crystal size in μ	250	200	300
Pleocroism of ppt. crystals	Weak (yellow)	Weak (yellow)	Intense (yellow, red, green)
Extinction angle	15-17°	90°	40°

Limiting ratios when reaction occurs in gas cell

NO_2^- : Cl^- (or Br^-, NO_3^-, SO_4^{2-}) = 1:100 for 1μg NO_2^-
NO_2^- : I^- (or CN^-, CNS^-, SO_3^{2-}) = 1:50 for 1μg NO_2
NO_2^- : S^{2-} = 1:25 for 1.5 μg NO_2^-.

Saturated solutions of 1,4-methylamino-or 1,4-ethylaminophenylmercuri-acetate (obtained according to [2]) in 6-8% acetic acid, form crystalline precipitates of the respective nitrosamines with nitrites in acetic acid solutions. It is possible to observe the appearance of crystals of the nitrosamines in a drop of the reagent placed on the lower side of the cover slide of the gas cell, 5-12 minutes after the acidification of the test solution. The crystals appear faster, the smaller the drop of reagent (Fig. 3[1] for the reaction product with 1,4-methylaminophenylmercuriacetate, Fig. 4[1] with 1,4-ethylaminophenylmercuriacetate). When 1,4-ethylaminophenylmercuriacetate is used, particularly in dilute solutions of nitrites, the reaction proceeds better, if 3-4 minutes after acidification of the drop of test solution, the cover glass of the gas cell is removed. The formation of crystals can then be observed 3-4 minutes after removal of the glass. A saturated aqueous solution of 1,4-ethylaminophenylmercuriacetate also forms crystalline precipitates with nitrite solutions, in the form of colorless prisms up to 60 μ. This reaction is very slow when a gas cell is used. Interfering ions (Cl^-, Br^-, I^-, CN^-, CNS^-, S^{2-}, SO_3^{2-}, SO_4^{2-}), must be removed beforeband by the method described above.

The limiting ratios for the reactions with 1,4-methylaminophenylmercuri-acetate in a gas cell are as follows:

NO_2^- : Cl^- (or Br^-, CNS^-, NO_3^-, SO_4^{2-}) = 1:100 for 1.6 μg NO_2^-
NO_2^- : I^- (or CN^-, SO_3^{2-}) = 1:50 for 1.6 μg NO_2^-
NO_2^- : S^{2-} = 1:50 for 3.2 μg NO_2^-

The limiting ratios for reactions with 1,4-ethylaminophenylmercuriacetate are half as much.

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[1]) See Plate, page 79.

A saturated aqueous solution of quinolinemercuriacetate (m.p. 155°) rapidly forms a crystalline precipitate of quinolinemercurinitrite (Fig.5)[1] with nitrites (in a gas cell). Under the same conditions but with an acetic acid solution of the reagent, the formation of a crystalline precipitate is considerably slower. In aqueous solution, without a gas cell the sensitivity of the reaction is higher; limit of identification 0.2 μg NO_2^- (in a gas cell it is 0.6 μg). The limiting ratios for reactions in a gas cell are the same as for the reactions with 1,4-ethylaminophenylmercuriacetate.

The crystals of reagents which settle out on the drying of a drop differ appreciably from the crystals of the reaction products of mercury organic compounds with nitrites. Results are given in Table 2 which characterize the crystals of 1,4-methylamino- and 1,4-ethylaminophenylmercuriacetate, and quinolinemercuriacetate which form on the drying out of drops containing them.

It should be noted that drops of the reagent solution dry out slowly in a gas cell and separation of crystals can be observed only after an interval of 10-12 hours.

Table 2

Characteristics of Reagent Crystals

	Reagent		
	1,4-methylamino-phenylmercuri-acetate	1,4-ethylaminophenyl-mercuriacetate	Quinolinemercuri-acetate
Color, form of reagent crystals	Colorless clusters of fine needles and small plates	Colorless clusters of plates	Colorless clusters of rods and plates
Pleochroism of the reagent crystals	Weak (yellow)	Weak (yellow)	Weak (yellow, red, green).
Extinction angle of crystals	90°	15-17°	90°

SUMMARY

1. A microcrystalloscopic reaction for nitrates with 1,4-aminophenylmercuriacetate is proposed. Some crystallo-optic constants of crystals of 1,4-aminophenylmercurinitrate are adduced. The limit of identification is 0.3 μg NO_3^-. This reagent can also be used for detecting nitrites by means of a gas cell, after oxidation of the NO_2^- separating out of an acid solution to NO_3^-.

2. Three reagents are proposed for the microcrystalloscopic identification of nitrites, namely, 1,4-methylamino- and 1,4-ethylaminophenylmercuriacetates and quinolinemercuriacetate. Some crystallo-optic constants are given for the respective nitrosamines and for quinoline mercurinitrite. The limits of identification when the reactions are carried out in a gas cell are 0.6-1.6 μg NO_2^-.

3. Ions which interfere with the reactions for the nitrates and nitrites (Cl^-, Br^-, I^-, CN^-, CNS^-, S^{2-}, SO_3^{2-}, SO_4^{2-}), are removed by means of Ag and Pb acetates, and the NO_2^- ions [illegible] by addition of ortho or metanitraniline, whereby the effect of excess interfering ions can be reduced.

Received May 31, 1950

[1]) See Plate, page 79.

LITERATURE CITED

[1] I. M. Korenman, Microcrystalloscopy (1947), p. 182, 191.

[2] F. Whitmore, Organic Mercury Compounds (1938), p. 188, 192.

[3] L. G. Makarova and A. N. Nesmeyanov, Synthetic Methods in the Field of Metallo-Organic Compounds of Mercury, (1945), p.45, 51, 53.

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NEW AZO-INDICATORS OF THE METHYL ORANGE SERIES, AND THE RELATION BETWEEN THE STRUCTURE AND pH CHANGES OF AZO-INDICATORS [1)]

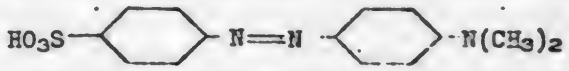
V. I. Kuznetsov and G. N. Kosheleva

Institute of Chemical Reagents, Moscow

At a time when intensive search is being carried out for new organic reagents for the detection of different metallic ions and new methods for developing such researches are being worked out, due attention is still not given to research for indicators for H^+ ions, i.e. pH-indicators. Meanwhile the demand for new pH-indicators, particularly for strong acid solutions is becoming urgent.

pH-Indicators of different structures possess unequal value in practice. Recently attention was given to one factor, to which little significance has been attached hitherto, namely, if the molecule of a pH-indicator contains even only two salt or complex forming groups, and these are disposed in such a manner that they can form cyclic salts with metal ions, then such a pH-indicator can under suitable conditions give color reactions with metals, which are quite appreciable even in very dilute solutions. The colors that develop in such a case distort the color of the pH-indicator and lead to a very substantial "salt effect of a special kind" [1]. Some pH-indicators tend in addition to give colored "solid phase" reactions [2], which also makes the indicators unsuitable in the presence of a number of elements.

These errors are not characteristic of azo-indicators which contain amino or hydroxy groups in the para position with respect to the azo-group, e.g. the substituted p-dimethylaminoazobenzene-p'-sulfonic acid (methyl orange).



The present investigation is devoted to a search for new pH-indicators among the substituted p-dimethylaminoazobenzene-p'-sulfonic acids.

There are some references to the study of the relation between structure and pH change for azo-indicators in the literature, e.g. Thiel [6], Blumberger [7] and Glockner [8].

In these investigations the values of the pH are compared with the structure, and values of the pH given for which the indicators are in the semi-acid form (pK). Unfortunately the conclusions from these investigations do not give a sufficiently clear picture to serve as a basis for a search for new pH-indicators with the given pH value changes.

The overall picture is as follows. The introduction of positive substituents ($-NH_2$, $-OCH_3$, $-OH$) increases the pK value somewhat, while the introduction of negative substituents ($-NO_2$, $-SO_3H$, $-COOH$) decreases the pK. But the extent of the shift is small, the interval between extreme pH values is only 0.5 pH units.

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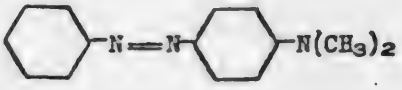
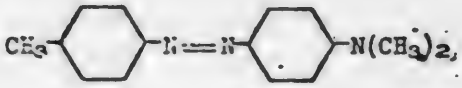
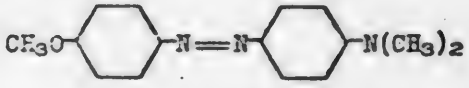
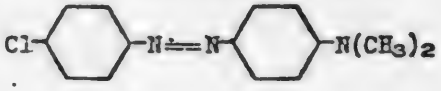
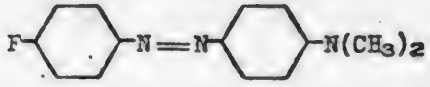
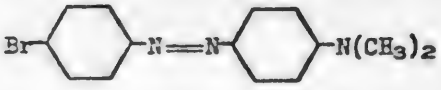
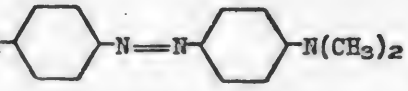
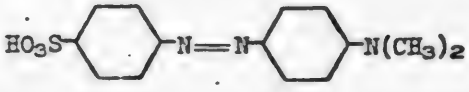
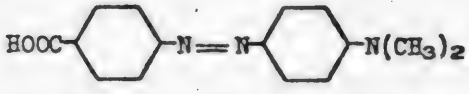
1) Extract from a dissertation by G.N.Kosheleva.

Our research on a series of substituted p-dimethylaminoazobenzenes showed that in this case the effects of positive and negative substituents, in general are similar and rather small in their absolute values (Table 1). Nevertheless we observed that strongly acid salt forming groups ($-SO_3H$, $-COOH$) do not decrease but actually increase pH.

Table 1

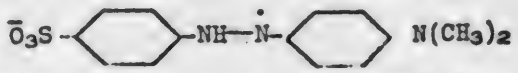
The Effect of Substituents on pK for Azo-indicators of the p-Dimethylaminoazobenzene Series

No.	Formula	pK in 50% alcohol	Magnitude of pK displacement in pH units as compared with No.1.
1		1.98	-
2		2.06	+0.08
3		2.15	+0.17
4		1.70	−0.28
5		1.68	−0.30
6		1.70	−0.28
7		1.72	−0.26
8		2.16	+0.18
9		2.10	+0.18

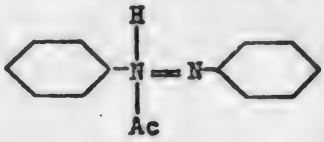
Thus for this particular series of pH-indicators the displacement of pK arising from the effect of positive and negative substituents in the para position to the azo group is small.

Greater displacements of pK can be achieved when other factors are considered.

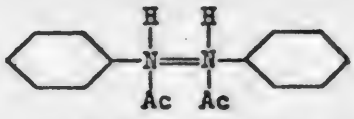
The change in color of aminoazo compounds in going from alkaline to acid media is connected with salt forming azo groups (formation of "azo salts"). Several methods of representing the azo-salts formed in acid solutions have been proposed and many hypotheses exist regarding their structure, e.g. V. Diltei and R. Vitsinger consider azo-salts to be compounds containing a coordinatively unsaturated nitrogen, and represent their structure as follows [3]:



F. Kerman proposes the following structures [4]:



or



(Ac = acid radical)

Whichever method may be used for depicting the structure of azosalts, it is clear that in order to facilitate the formation of azo-salt, the azo-group must be opened up, while none of the substituents which are spatially near to the azo-group should impede the approach of the proton to the nitrogen of the azo-group.

From this point of view, the presence of substituents near the azo-group should impede salt formation and therefore lead to a decrease in the value of pK.

Experiment showed that this actually occurs. By the introduction of groups which sterically hinder salt formation of the azo-group the pK value is decreased. The absolute value of the decrease in pK in this case is considerably greater than that which results from the introduction of the negative substituents mentioned above in other positions in the molecule of the azo-compound. Steric hindrance as a result of substituents is most clearly manifested for the case of indifferent substituents, since the influence of other factors is not superimposed on their action. But substituents in the ortho position to the azo-group exert a definite effect on pK whatever the nature of the substituent.

The relation mentioned above is shown very clearly here. Salt-forming substituents in the ortho position to the azo-group, do not decrease pK, in contrast to non-salt-forming substituents, but on the other hand increase it. It is possible that salt-forming substituents facilitate proton donation to the azo-group and therefore azo-salts are formed in less acid solutions.

This method of lowering pK by a considerable amount enables a series of new pH-indicators to be synthesized for low pH values.

In the present article we shall describe new pH-indicators of the methylorange series. New indicators of the tropeoline OO series (diphenylamine substituted-<4-azo-1>-benzene-4-sulfonic acids) described by G.N. Kosheleva in her dissertation are also very interesting.

TABLE 2

Effect of Substituents in the Ortho Position to the Azo Group on pK

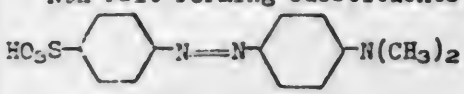
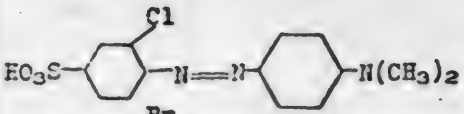
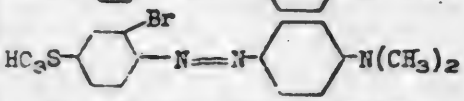
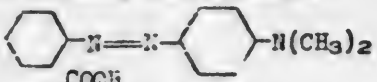
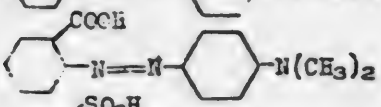
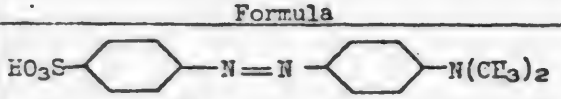
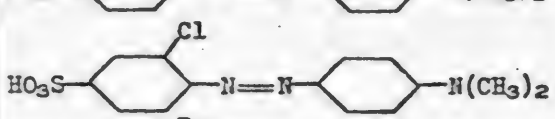
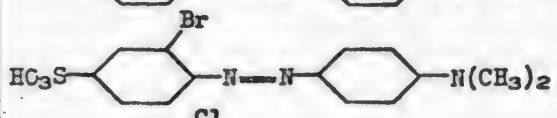
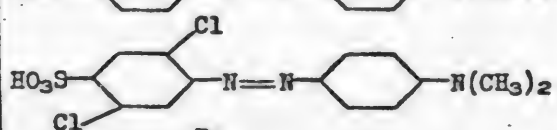
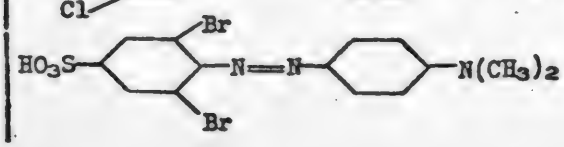
No.	Formula	pK	Magnitude of pK shift as compared with No. 1– in pH units
	Non salt-forming substituents		
1		3.37	–
2		2.70	−0.67
3		2.73	−0.64
	Salt Forming Substituents		As compared with No. 4
4		3.28	—
5		5.40	+3.12
6		3.85	+0.57

TABLE 3

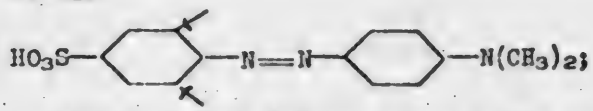
New Indicators of the Methylorange series; Acid solutions - rose, neutral and alkaline - yellow

No.	Formula	pK	Range of pH change in pH units	Range of pH change in N HCl
1		3.37	3.1-4.5	0.00005-0.001
2		2.70	1.6-3.7	0.025-0.00020
3		2.73	1.6-3.6	0.025-0.00025
4		2.3	1.4-3.2	0.04-0.001
5		-	-0.5	-0.4

The deliberate use of steric hindrance can serve as a guide for improving the selective action of analytical reagents. We shall discuss these ideas in a special article.

New pH-Indicators of the Methylorange Series

The new indicators of this series which are described differ from methyl orange.



in that they have halogen atoms in the positions indicated by the arrows.

These indicators closely resemble methylorange externally. They are soluble in water and form colors which are similar to that of methylorange, yellow in neutral and alkaline media and rose in acid.

Different stable imitative colors, e.g. colors of solutions of iron and cobalt salts, proposed by Kolthoff or Taube [5], which are used for comparison with methylorange can therefore be used for the new indicators. The pH values of course are different.

These indicators also resemble methylorange in that they are free from some salt errors which arise from the presence of traces of multivalent elements [1], and also like methylorange they do not easily tend to give colored solid phase reactions [2] and therefore are suitable for all kinds of inorganic analysis.

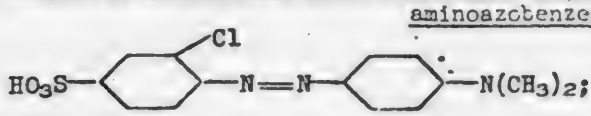
The colors formed by the new indicators are completely stable both in alkaline and in acid solution and in this connection possess a definite advantage over some other indicators used for low pH values such as methylviolet and malachite green, the colors of which in acid solution are quickly decolorized and tend to give colored solid phase reactions with heavy anions, so they are unsuitable in many cases.

In addition, the colors of the new indicators, like that of methylorange, can if necessary be easily destroyed by strong reducing and oxidizing agents (elemental Br, Cl, $KMnO_4$). H_2O_2 has no effect on the indicators.

The pK values and the range of pH changes for these indicators are given in Table 3.

The new indicators cannot be prepared by direct bromination or chlorination of methylorange, but are easily synthesized by the methods described below.

Synthesis of New pH-Indicators of the Methylorange Series 2-Chloro-4'-Dimethylaminoazobenzenesulfonic Acid-4



$C_{14}H_{14}O_3N_3ClS$ (M = 339.8)

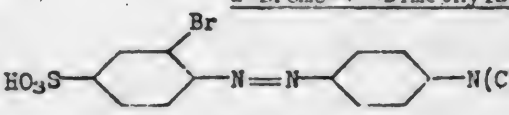
A solution of 4.5 g of o-chloroaniline-p-sulfonic acid in the form of its Na salt and 1.6 g $NaNO_2$ in 5 ml H_2O are poured into a mixture of 10 ml conc.HCl and 15 g ice. 2.6 g dimethylaniline in 10 ml dil. HCl (1:2) is added to the suspension of diazonium salt obtained and to the final mixture a conc.solution of Na-acetate is added dropwise with stirring, till there is no further acid reaction to Congo paper.

The 2-chloro-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out

is filtered off and is twice recrystallized from alcohol. The crystals are orange.

5.310 mg substance: 0.499 ml N_2 (753 mm, 21°)
4.300 mg substance: 0.417 ml N_2 (753 mm, 21°)
Found % N: 10.81, 11.07
$C_{14}H_{13}O_3N_3ClSNa$. Calculated % N: 11.01

2-Bromo-4'-Dimethylaminoazobenzenesulfonic Acid-4



HO_3S—(Br)—$N{=}N$—$N(CH_3)_2$; $C_{14}H_{14}O_3N_3BrS$. (M = 284.3)

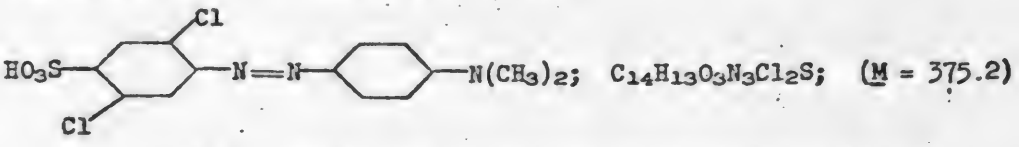
A solution of 4.1 g o-bromosulfonic acid as its Na salt and 1 g of $NaNO_2$ in 30 ml H_2O are poured into a mixture of 5 ml conc. HCl and 20 g of melting ice. The diazonium suspension formed is poured into a solution of 1.8 dimethylaniline in 10 ml alcohol. After 1 hour standing the product which separates out is filtered and recrystallized first from H_2O and then from alcohol. The crystals are yellow-orange in color.

4.745 mg substance: 0.446 ml N_2 (756 mm, 22°)
4.670 mg substance: 0.436 ml N_2 (757 mm, 22°)
Found % N: 10.83, 10.73
$C_{14}H_{13}O_3N_3BrSNa$. Calculated % N: 10.93

2,5-Dichloro-4'-Dimethylaminoazobenzenesulfonic Acid-4

A solution of 1.1 g of dichlorosulfanilic acid as the Na salt in 10 ml H_2O and 0.3 g of $NaNO_2$ are poured into a mixture of 10 ml conc. HCl and 10 g melting ice. The suspension of diazonium salt thus obtained is gradually added with stirring to 0.51 g of dimethylaniline dissolved in 5 ml alcohol and mixed for 1 hour. The 2,5-dichloro-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out is filtered and dried. The yield was 2 g and it was recrystallized from H_2O and alcohol. The crystals were of an orange-yellow color.

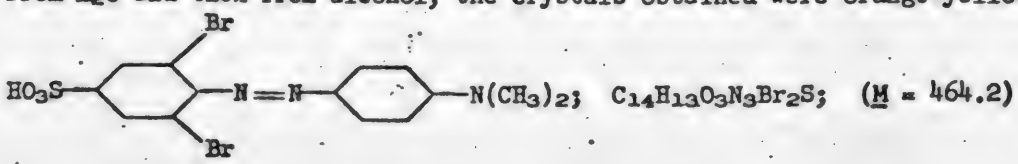
0.2034 g substance: 16.34 ml 0.1 N HCl
0.1536 g substance: 12.26 ml 0.1 N HCl
Found % N: 11.24; 11.17
$C_{14}H_{12}O_3N_3Cl_2SNa$. Calculated % N: 11.19



HO_3S—(Cl, Cl)—$N{=}N$—$N(CH_3)_2$; $C_{14}H_{13}O_3N_3Cl_2S$; (M = 375.2)

2,6-Dibromo-4'-Dimethylaminoazobenzenesulfonic Acid-4

A solution of 1.5 g dibromosulfanilic acid as its Na salt in 10 ml H_2O and 0.3 g $NaNO_2$ are added to a mixture of 10 ml conc. HCl and 10 g melting ice. The suspension of diazonium salt thus obtained is added gradually with stirring to a solution of 0.51 g dimethylaniline in 15 ml alcohol. After 1 hour's mixing the 2,6-dibromo-4'-dimethylaminoazobenzenesulfonic acid-4 which separates out is filtered off. The weight of product obtained was 1.9 g. After recrystallization from H_2O and then from alcohol, the crystals obtained were orange-yellow in color.



HO_3S—(Br, Br)—$N{=}N$—$N(CH_3)_2$; $C_{14}H_{13}O_3N_3Br_2S$; (M = 464.2)

4.830 mg substance: 0.404 ml N_2 (730 mm, 22°)
5.250 mg substance: 0.442 ml N_2 (754 mm, 23°)
Found % N: 9.11, 9.35
$C_{14}H_{12}O_3N_3Br_2SNa$. Calculated % N: 9.10

SUMMARY

1. The introduction of positive ($-NH_2$, $-OCH_3$) or negative ($-NO_2$, $-COOH$, $-SO_3H$) substituents in the meta or para position to the azo group in the molecule of p-dimethylaminoazobenzene p-sulfonic acid (methylorange) gives rise to only a relatively insignificant displacement of pK.

2. A considerably greater shift is observed in pH when indifferent substituents (-Cl, -Br), giving rise to steric hindrance are introduced into the ortho position relative to the azo-group.

3. The new indicators described are chloro- or bromo-substituted methylorange; they are similar to methylorange in color, but are suitable for more acid solutions, pH 1.6 to 3.7.

4. The syntheses of some new pH-indicators are described.

Received July 31, 1951

LITERATURE CITED

[1] V.I.Kuznetsov, J.Anal.Chem. 5, 365 (1950).

[2] V I.Kuznetsov, Prog.Chem. 18,75 (1949); Proc. Acad. Sci. USSR, 41, 113 (1943).

[3] R.Vitsinger, Organic Dyes. Introduction to the chemistry of dyes on the basis of the coordination theory. Leningrad, 1936, p. 46.

[4] Kehrmann, Ber. 48, 1933 (1913); 41, 2340, 3396 (1908).

[5] E.Mislovitser, Determination of the Concentration of Unlike Ions in Liquids. Leningrad, 1932. Pp. 368-70.

[6] Thiel, Z. anorg. .Chem. 173, 169 (1928).

[7] Blumberger, Rev.trav.chim. 59, 665-674 (1940).

[8] Glöckner, M. 80, 493 (1949).

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Obituary

MIKHAIL MAKSIMOVICH FAINBERG

Mikhail Maksimovich Fainberg, a member of the Commission on Analytical Chemistry in the USSR Academy of Sciences, died on the 14th of October 1951. His was an untimely death.

Since he was one of the foremost specialists in the field of gas analysis, Fainberg spent the last years of his life as a scientific instructor in one of the divisions of the Ministry of Chemical Industry.

His erudition and energy were manifested in his all-round scientific activity. Apart from his main work, he lectured on automatics to workers of the Ural factories, and acted as a consultant in the Laboratory of Automatization of the Ukrainian State Institute of Applied Chemistry and in the Institute of Automatics and Telemechanics in the USSR Academy of Sciences.

His textbook on "Automatic Gas Analyzers" is the only work in Russian on this question.

His work in the field of automatic control gained him wide popularity and his activity as an inventor resulted in the introduction of new methods and apparatus into automatic control for our industries. The majority of his 25 inventions are used in industry.

Some of his inventions which are used industrially are: a portable gas analyzer for determination of fuel gas; an apparatus for continuous analyses of fuel gas; a thermochemical gas analyzer for automatic determination of oxygen in fuel and inert gas; an electrochemical gas analyzer for automatic determination of sulfur dioxide; an apparatus for automatic determination of traces of oxygen in gases; etc.

While maintaining a close connection with industrial workers, Fainberg at the same time paid considerable attention to the popularization and clarification of questions of automatic control, and published more than thirty papers in the course of his work.

In 1943 Fainberg was awarded the degree of Candidate of Chemical Sciences.

The fruitful scientific activity of Fainberg was marked by high Government awards. In 1942 he was awarded a Stalin prize and in 1942 the Order of the Red Banner of Labor.

In the person of Mikhail Maksimovich Fainberg the Commission on Analytical Chemistry of the USSR Academy of Sciences, of which he was an active member, has suffered a grievous loss.

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RESOLUTIONS OF THE CONFERENCE ON CLASSICAL METHODS OF CHEMICAL ANALYSIS IN THE GEOCHEM INSTITUTE OF THE USSR ACADEMY OF SCIENCES, HELD IN MOSCOW ON THE 14-17TH OF NOVEMBER 1951

Russia is the birthplace of new paths in analytical chemistry, where both the classical methods of chemical analysis and its theoretical bases have been developed. This indisputable fact is deliberately belittled by foreign scientists. Some of them indulge in direct falsification of the history of chemistry in our country so as to deny the priority of our scientists.

The brilliant investigations of M. V. Lomonosov laid the foundation of chemical analysis just like those of D.I.Mendeleev and A.M.Butlerov, who by their work created an epoch in the development of world science, and strengthened the theoretical basis of analytical chemistry, leading to a wide generalization and the creation of new paths.

To such paths created by our fellow countrymen belong: the development and application of organic reagents in chemical analysis (M.A.Ilinsky and L.A.Chugaev); the development of physico-chemical analysis (N.S. Kurnakov); chromatographic analysis (M.S.Tsvet); microcrystalline analysis (M.V.Lomonosov, T.E.Lovits); crystallo-optical analysis (E.M.Fedorov); spot tests and special tests for metals and alloys (N.A.Tananaev), etc.; N.A.Menshutkin produced the first classical textbook on analytical chemistry.

A new era in analytical chemistry developed after the October Revolution. Thanks to the concern of the Bolshevik Party, the Soviet Government and of Comrade Stalin personally, a turbulent growth of scientific investigation, in factory and university chemical laboratories started. Reagert chemistry has become an industry in itself; general laboratory and precision apparatus are being produced and large numbers of books and journals on analytical chemistry are being published; conferences and meetings devoted to this branch of knowledge are regularly held; a firm link has been established between theory and practice, while the development of the theory and practice of analytical chemistry has attracted large collectives. Soviet analysts actively participate in the building of Communism and help its constructions.

Soviet analytical chemistry which develops on the basis of Marxist-Leninist methodology and endeavors to bring contemporary analytical methods to bear on the problems which face our Socialist constructions, has attained important successes and occupies a leading place in world analytical chemistry.

The Conference on Classical Methods of Analysis, convened by the Commission on Analytical Chemistry of the Geochem Institute at Moscow was marked by the intense activity of the participants. Reports were read which reflect the different approaches in the development of contemporary analytical chemistry. Delegates from 29 cities in the USSR were present including those from Leningrad, Kiev, Saratov, Alma-Ata, Ivanov, Gorky, Kharkov, Lvov, etc.

It was noted at the conference that Soviet chemical analysts have attained considerable success in a number of fields, e.g. the application of the physico-chemical analysis of N.S.Kurnakov to the solution of analytical problems; the study of ionic equilibrium; the application of ionic energetics; the development of the theory of the action of organic reagents, their wide study and use in

inorganic analysis; the study of oxidation-reduction processes, etc.

Particular attention was paid to the question of anomalous separation of elements, especially the phenomenon of coprecipitation.

Systematic studies are being carried out on the study of complex compounds and their application for developing new analytical methods.

A number of investigations devoted to the establishment of regularities in ionic reactions in connection with Mendeleev's periodic law should be noted.

A series of successes has been attained in working out new methods of volumetric and gravimetric analyses and improving those already in use, in the development of micro and semi-micro methods, and in the application of ion exchange in the development and improvement of electroanalytical methods, etc.

New methods of making weights have been worked out, in particular by the application of the inverse link method.

At the same time the conference made a note of a number of deficiencies.

The most important are the following: insufficient further development of new developments in the field of gravimetric, volumetric and electrical methods of anelysis, in the field of work on the separation of elements by extraction and absorption methods, and in precipitation by organic reagents, particularly the use of complex-compound formers which act selectively; the slow introduction of new oxidation-reduction and other indicators; the lag in adoption and use of a number of thecretical principles in analytical chemistry developed by Soviet scientists. The analysis of organic materials is weakly developed. Little attention has been given to working out the methods of "phase" analysis of mixtures and the determination of elements of different valencies when they occur together.

The output of weights for macroanalysis is insufficient. The output of semi-micro and micro weights is insufficient to satisfy the increasing demands of scientific-investigational and factory laboratories.

The necessary amount of general laboratory apparatus for semi-micro and micro analysis is not forthcoming; this hinders the development and introduction of new analytical methods into laboratory practice.

The decrease in the number of hours set apart by educational institutions for teaching analytical chemistry, lowers the general standard of scientific training of chemists. The training of average analytical personnel-laboratory workers and preparators in a number of branches of industry is completely unsatisfactory.

The low rate of publication of books on different theoretical and practical questions in analytical chemistry and of journals leads to a considerable delay in the publication of work, including work connected with the priority of Soviet scientists.

The coordination of the work of analysts and its application to the great schemes of Communism is still weak. Work on the unification and standardization of methods of technical analysis has slowed down considerably and in some cases stopped completely. This leads to a considerable difference between the scientific-experimental level of these methods and the contemporary possibilities of analytical chemistry, and this is reflected in the state of the control of production.

The conference regards it necessary to recommend the following measures:

1. To continue to strengthen the link between scientific workers in analyt-

ical chemistry with production, with special reference to increasing the help to the great constructions of Communism, and coordinating the work of different institutions in this field. To ask the Division of Chemical Science of the Academy of Sciences USSR to consider this question and to issue the necessary recommendations.

2) To call regional conferences to attract workers from factory laboratories in order that new methods of analysis can be introduced into factory practice and to generalize the experience of Stakhanovite methods of work.

3) To regard it a necessity to strengthen the links between the Commission on Analytical Chemistry with outlying districts by participation of the Commission in regional meetings and holding All Union meetings not only in Moscow but in other cities also.

4) To ask the Commission to bring about the coordination of scientific work on analytical chemistry carried out in different scientific institutions in the Soviet Union.

5) In the development of the theory and practice of classical methods of analysis, the conference deems it necessary

a) to direct attention to the development of work on the theory of solutions and the solubility of precipitates as applied to analytical chemistry; and to the expediency of holding a special meeting for discussion of these questions

b) to recommend further continuation and expansion of theoretical work along the directions indicated at the present conference; in particular, the application of physico-chemical methods of analysis to the study of systems which are important analytically; the phenomenon of coprecipitation; the thermodynamics of analytical reactions; the application of the periodic law to the fundamental characteristics of ions; the study of organic reagents and their application in analytical chemistry; oxidation-reduction reactions and complex formation; the application of ionites (cationic and anionic exchange resins); new methods of volumetric analysis; group analysis and other rapid methods; electrolysis with the mercury cathode; and the use of statistical methods in evaluating analytical results.

6) In connection with the continuously mounting importance of organic reagents in analysis and the absence at the present time of systematic information about new reagents, as a result of which valuable new reagents do not come into general use for a long time, the conference regards it essential:

to organize within the Commission on Analytical Chemistry a special section for new analytical reagents which, with the participation of the All Union Scientific-Experimental Institute of Chemical Reagents, will consider the value of all the new reagents described, and publish its opinion and its recommendations regarding these reagents.

7) To deem it necessary to hold systematic reviews of the unification and standardization of technical analytical methods with the widespread use of the experience of factory laboratories and research institutes.

8) To continue and expand work on the history of analytical chemistry in our country, to expose foreign scientists engaged in falsification in this connection. To accelerate the publication of monographs on the history of analytical chemistry.

9) To deem it necessary to publish monographs on different topics in analytical chemistry such as: the application of physico-chemical analysis to analytical chemistry; the theory of the action and application of organic rea-

gents; the methods of mathematical statistics in analysis; and thematic collections on special topics in analytical chemistry.

10) To regard it as urgent to increase considerably in the near future the size of the Journal of Analytical Chemistry, because of the hold up in publishing work which often leads to loss of priority for Soviet analysts and hinders the introduction of new and improved methods of analysis in industry.

11) To regard as a necessity the renewal of the publication of chemical reference journals together with a general improvement and increase in annotated bibliographic work with indexes to work in analytical chemistry, printed in different collections.

12) To ask the Ministry of Higher Education to increase the amount of time devoted to teaching analytical chemistry and to reissue a number of books in analytical chemistry.

13) To direct the attention of the Ministry of Machine and Apparatus Construction to the unsatisfactory position which exists with regard to the output of analytical weights, including the application of return communication, particularly for micro and semi-micro analysis.

To ask the Ministry of Machine and Apparatus Construction to suggest to organizations who supply microweights and other apparatus, that they establish closer contact with the Commission on Analytical Chemistry at the Geochem Institute of the USSR Academy of Sciences and not to issue new models of weights without the approval of this Commission.

To organize the preparation of new ion exchange resins.

14) To ask the Ministry of Chemical Industry to expand the production of chemical apparatus and reagents already in use, and also to familiarize the issue of new reagents by lists, approved by the Commission on Analytical Chemistry.

15) To deem it necessary to call a conference on the application of marked atoms; on the chemical side of spectral analysis; the application of organic reagents; on the polarographic and chromatographic methods; the analysis of organic compounds; and also on rapid and automatic methods.

16) To consider the state of terminology in analytical chemistry and to draw up the necessary recommendations.

17) To consider it essential to call a second All Union Conference on Analytical Chemistry soon.

18) To publish the material of the present conference in the form of a separate thematic collection "Work of the Commission of Analytical Chemistry"; to publish the resolutions of the conference in the next numbers of the "Journal of Analytical Chemistry."

Criticism and Bibliography

A. K. Babko and A. T. Pilipenko, "COLORIMETRIC ANALYSIS".
State Chemical Press, Moscow-Leningrad 1951, 408 pp. Price 20 rubles.

A. K. Babko and A. T. Pilipenko's textbook on colorimetric analysis is one of the first books planned for publication from a series of Russian monographs and manuals on analytical chemistry. This book, which has appeared at a very opportune moment, was designed to fill a serious gap in our literature on colorimetric analysis. In its makeup the book is original and new.

The book is divided into three parts.

The first part is devoted to description and consideration of the conditions necessary for converting the component to be determined into a colored compound. The general laws of light absorption by colored solutions are considered. A considerable amount of information regarding Beer's law, the effect of pH on colorimetric determinations, and the colorimetric determination of complex mixtures is adduced. A section is included here on extraction, in which the extractive separation of the elements is described, apparently in more detail than in any previous textbook on analytical chemistry. The valuable contributions of Babko himself on the deviations from Beer's law are included here as well as his work on the influence of pH on the color, and the ionic composition in solution, etc. On reading this part one feels the easy approach of the authors to the questions of the calculations of different constants, equilibrium ionic concentrations, etc.

In its abundance of theoretical material and depth of approach, the first part of this book is better than the corresponding section of any other textbook on analytical chemistry.

The second part is devoted to consideration of the methods of measuring color intensity and the requisite apparatus. Here, in addition to test methods, the construction and method of operating the visual and photoelectric colorimeters as used in many laboratories are treated in sufficient detail. A special chapter is devoted to the colorimetric determination of mixtures of two colored components.

The third and longest part, which occupies more than half the book, contains descriptions of special methods of colorimetric determination. The material is arranged not according to elements, but in chapters (13 headings) which describe the determination of elements forming related colored compounds. The following groupings are employed: thiocyanate and halogen complexes; the use of NH_3 and organic bases; peroxide compounds; determination of F by weakening of the color; heteropolyacids; inner complex compounds; compounds with dyes containing OH-groups, with organic reagents containing N_2, with organic reagents containing SH groups; methods based on oxidation-reduction methods; the syntheses of organic colored compounds, and methods of determination of pH.

Although we are not happy with regard to the choice of the groups and the relation of the different methods, particularly those connected with the application of organic reagents, to one group or another, we must admit that such a scheme, of course, is more convenient than the method of arrangement according to elements as used in other textbooks. By means of this group arrangement the mechanism of a reaction as well as its selectiveness is emphasized more clearly and results in a greater economy of printing space.

In each chapter separate descriptions are given of the determination of individual elements. Each description is made up on the same model. First, a general description is given which includes information on the theory or idea of

a reaction, and indicates the factors which interfere with the reaction and gives the method of measuring the color and the sensitivity of the reaction. Further, a fairly detailed description is given which includes a brief description of the method, a list of the necessary reagents, and the procedure. Several procedural methods are given for each element; for determinations of the element in pure solutions and in different materials. The literature references are given as footnotes.

By holding strictly to this method of description the book is suitable for use and gives a pleasant impression.

The book is well written, in simple and clear language. It gives the impression of being a reliable textbook, carefully compiled on a strictly scientific basis with due regard to practical considerations.

Although we have thus far given a good review of this book, there are nevertheless some debatable points both of a general and particular character which it is necessary to observe.

In agreeing to write a book on colorimetric analysis in such a small volume (400 pages) the authors took on a thankless task. To give anything like a complete coverage to a subject which is expanding so rapidly at the present time in such a small book is obviously impossible. Therefore the authors had to resort to selection of material which they thought to be of the greatest interest. Naturally different opinions exist with regard to the best selection; e.g. it is not clear why the authors omitted the very useful diethyldithiocarbamate method of estimating Cu while they included the rather insensitive dimethylglyoximepyridine method which necessitates the use of silver nitrate and is a method in which many metals as well as chlorides interfere.

In some places references are made to other methods for the determination of various elements which are not described, but references to the best variants of these other methods are not always given. The question of how to find these best methods in the literature therefore arises.

Colorimetric methods of determining S, Sn, Br, I, Ag, Ca, Cd, Na and a large number of the so-called "rare" elements, Zr, B and others are not described. It would be useful if the authors in their preface explained their motives for choosing the elements and the methods of determining them as they have.

All the textbook, as the authors themselves observed in the preface, is compiled on the basis of Russian literature only. Throughout the book there are only 14 references to the works of foreign scientists. The motives here are not clear either. If good, reliable colorimetric methods for the determination of any element are described in foreign literature, it is not clear why they should not be included in this book.

The authors' views on the influence of pH, and on the conditions of formation of complexes between the different elements and organic reagents which are weak acids (salicylic acid, etc) are very debatable. In this connection the authors almost without reservation show a one-sided approach in which they assume that the conditions for the existence and the formation of complexes are determined solely by the concentration of the anions of the corresponding weak acids, which can be easily calculated on the basis of the dissociation constants of these acids. The nature of the cations, the effect of pH on the state of the cations and other factors relating to the elements are not considered (pp. 60, 64, 72, 161, 166, 240, 295).

When such an approach is used it is possible to reach an unexpected conclu-

sion, that apart from the dependence on the nature of the element, the complexes formed by the element are less stable, the higher the acidity, since according to the increase in acidity the concentration of the complex-forming compound decreases. This is approximately what the authors found (pp. 60, 166 and particularly 240, 295).

In this connection also the authors are faced with the difficulty of explaining the precipitation of elements of the 5th group by H_2S only from strongly acid solutions, in which the concentration of the anions SH' and S'' are very small; of explaining the high stability to acids of the salicylate complexes of Cr^{III}, which is considerably greater than that of the corresponding complexes of Al; or of explaining the capacity of B or Ge to form complexes with hydroxyanthraquinone in concentrated acid media. This one-sided approach of the authors is even more difficult to understand, when there exist works which are undoubtedly known to the authors (e.g. articles in the Journal of Analytic Chemistry, 2, 67 (1947); and the Journal of General Chemistry, 20, 807, 816 (1950);[1]) in which the unequal effect of pH on the capacity of an element to form complexes according to the nature of the element has been clearly demonstrated.

It is of course impossible to include all the methods of colorimetric analysis in such a small book. The authors should immediately undertake a second, considerably expanded edition of their textbook, in which they can eliminate errors which have crept in, and include any useful material left out of the first edition. We wish them luck.

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[1]) See Consultants Bureau English translation, pp. 845, 853.